THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

STUDIES OF POLYISOBUTENE AND CHLORINATED DERIVATIVES.

by

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STUDIES OF POLYISOBUTENE AND CHLORINATED DERIVATIVES.

SUMMARY

The contents of this thesis can be divided into two major topics of study; these are the measurement of low unsaturations in polyisobutene and the study of the thermal degradation of polyisobutene and chlorinated derivatives. Considerable use was made of radiochemical techniques since radiochlorine was involved in both studies.

The basis of the method of measuring unsaturation was to react the unsaturated compound with radiochlorine (chlorine-36) and to measure the amount of chlorine incorporated by counting techniques. Polyisobutene was studied in order to verify that the unsaturation was situated in the end-groups and was derived from the termination step of the cationic polymerisation process. The estimation of these postulated terminal double bonds in high polymers has not previously been attempted on a quantitative basis since conventional methods of analysis are not sufficiently sensitive. In order to convert chlorination results into meaningful values of unsaturation, the stoichiometry of the chlorination of branched double bonds was examined by studying model olefins and

polyisobutene of relatively high unsaturation which could be measured by other methods. It was concluded that true values of unsaturation could be obtained on the assumption that double bonds in polyisobutene reacted with one molecule of chlorine by a substitution mechanism by which one chlorine atom was incorporated per double bond. The terminal nature of the unsaturation was demonstrated by the fact that the molar unsaturation was inversely proportional to the molecular weight of the polymer. The degree of unsaturation was correlated with that postulated from cationic theory, thus providing a quantitative proof of theoretical and qualitative predictions.

The thermal degradation of polyisobutene was reviewed as a prelude to the study of chlorinated polymers. Experimentally, emphasis was placed on pressure methods rather than weight-loss techniques. It was shown that the rate characteristics were independent of the molecular weight of the starting polymer and that a rapid decrease in the rate of degradation initially was followed by a more gentle decrease. The kinetic data were supplemented by molecular weight studies and the results examined with respect to various modes of decomposition. It was concluded that the degradation was partly random in nature but deviated from random theory because structural factors favoured intramolecular transfer reactions, the predominance

of which influenced the product distribution and the rate characteristics. The presence of weak bonds in the chains was suggested as a possible reason for the high initial rate.

Chlorinated polymers were prepared by treating polyisobutene in carbon tetrachloride solution with chlorine at 60°C. The proton magnetic resonance (P.M.R.) spectra of the products showed that substitution occurred in both the methyl and methylene groups but, since the presence of some dichlorinated methylene groups was also indicated, the chlorine distribution was not entirely random. A preliminary study of the degradation by temperature-programmed techniques showed that the chlorinated polymers were less stable than the parent polymer and that even minute amounts of chlorine had a marked effect on the degradation behaviour.

Isothermal studies of the degradation characteristics were made at 190-240°C, approximately 100C° lower than for the polyisobutene studies. Since the volatile products were radioactive, counting apparatus was incorporated into the degradation assembly in order that the liberated chlorine might be estimated radiochemically. Most of the chlorine consisted of hydrogen chloride but there were traces of other products; isobutene was detected in product mixtures, especially those derived from polymers of low chlorine content.

Kinetic curves showing the build-up of chlorine in the volatiles against time revealed that the rate of chlorine evolution decreased rapidly from an initial maximum and reaction ceased before all the chlorine in the polymer was liberated. The kinetic order of the data was obscure but an order of 3/2 - cf. the degradation of poly(vinyl chloride) appeared to be applicable to at least part of the degradation curves. The activation energy found from the initial rates of degradation was approximately 30 k.cal.mole.$^{-1}$ Comparison of the initial rates for polymers of different chlorine content showed that the initial rate at 190-200°C was highest for the polymers of low chlorine content. This was explained in terms of steric hindrance to the migration of chlorine atoms during the abstraction of hydrogen atoms and in relation to the number of free methyl or methylene groups available for hydrogen abstraction. Several features, such as the mechanism by which the polymers became yellow on degradation and the reason why only part of the chlorine content was liberated on degradation, remained unsolved. It was concluded that much of the difficulty in elucidating these problems was attributable to the fact that these polymers were not multiples of simple, identical units, but consisted of a mixture of various chlorinated structures.

PREFACE.

The work described in this thesis was carried out in the period October 1963 to August 1966 at the University of Glasgow in the Department of Physical Chemistry, which is under the supervision of Professor J.M.Robertson, C.B.E., F.R.S.

I am indebted to the Science Research Council for the award of a Research Studentship, during the tenure of which this work was performed.

My thanks are also due to my colleagues in the Macromolecular group for useful assistance and discussion, and to various members of the technical staff of the Chemistry Department, in particular Messrs. R.Smith and G.Perrit, and Mrs.F.Lawrie.

Finally, I wish to thank Dr.I.C.McNeill for his general supervision and constant encouragement throughout my work.

Robert M'Guchan

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CHAPTER 1.

INTRODUCTION.

The work subsequently described in this thesis can be divided into two major topics of study. These are the measurement of low unsaturations in polyisobutene and the study of the thermal degradation of polyisobutene and chlorinated derivatives. The two fields of study, which might be surmised to be distinct apart from the use of the same polymer, had a common factor in the experimental approach made to the problems. Radioactive chlorine was involved in both studies and use was made of radiochemical techniques. Thus, the reaction between double bonds and radioactive chlorine formed the basis of measuring low unsaturations. In the second topic, main-chain chlorinated polymers were prepared by substituting hydrogen atoms in the polymer backbone with radiochlorine. The degradation behaviour of these polymers was investigated radiochemically by examining the products of degradation for radioactive chlorine content.

UNSATURATION IN HIGH POLYMERS.

Polymeric materials can be regarded as long chains or networks built up from simple units derived from the monomer. The degree of unsaturation may vary from high values to extremely low or zero values depending on the nature of the monomer(s) and the polymerisation processes used to make the polymer. High unsaturations are observed in polydienes in which each chain unit in the polymer retains one double bond, e.g.

$$n(CH_2{=}CH{-}CH{=}CH_2) \longrightarrow \text{-}(CH_2{-}CH{=}CH{-}CH_2)\text{-}_n$$

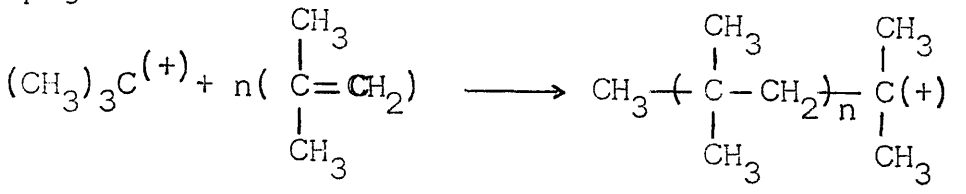
Butadiene — Polybutadiene

The polymerisation of mono-olefins, however, may produce saturated chains in which the degree of unsaturation is zero. It has been found, however, that many polymers of mono-olefins are not completely saturated, and they exhibit small degrees of unsaturation. The mechanism of the cationic polymerisation of isobutene[1] illustrates one source of low degrees of unsaturation:-

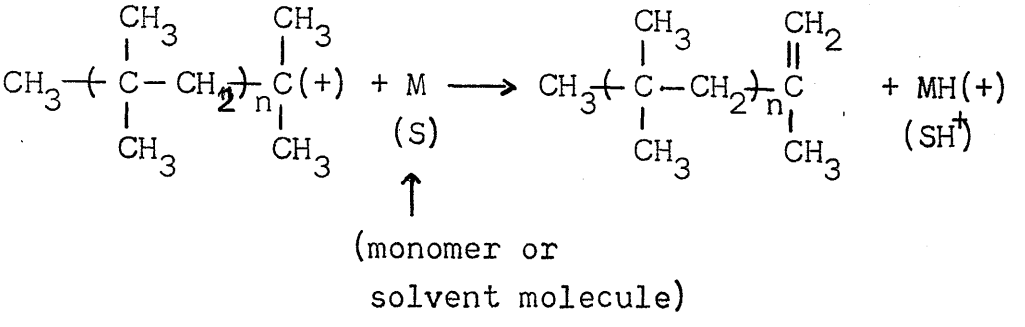
Initiation:

$$\begin{matrix} CH_3 \\ | \\ C{=}CH_2 \\ | \\ CH_3 \end{matrix} + SnCl_4.H_2O \longrightarrow (CH_3)_3C(+) + SnCl_4OH^{(-)}$$

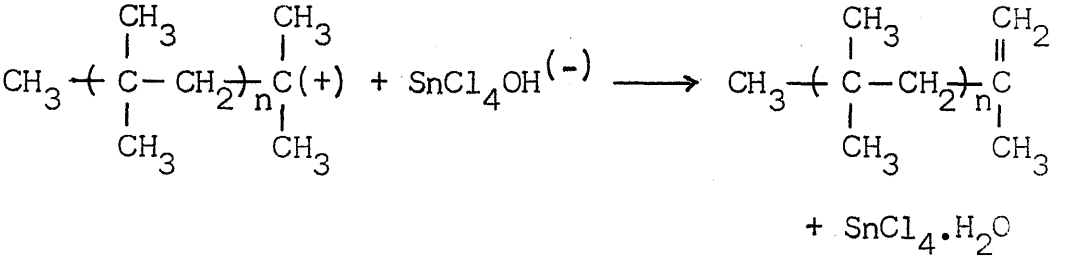
Propagation:



Transfer:



Termination:



This reaction scheme does not necessarily represent the complete picture, but it does show how terminal unsaturation may arise in polymers prepared by a cationic mechanism. Terminal unsaturation is also produced in the free-radical mechanism[2] of polymerisation by transfer and disproportionation reactions. A good example of this is provided by the polymerisation of methyl methacrylate at

60°C in which disproportionation produces unsaturated end structures in approximately 50% of the polymer chains.[3] Small amounts of internal unsaturation in polymer chains could result from abnormal propagation steps or from side-reactions of the polymer during the polymerisation process. Degrees of unsaturation intermediate between the high and low values are found in copolymers in which one of the monomers used is a diolefin. Thus, in isobutene-isoprene copolymers (butyl rubber) and in styrene-butadiene polymers (GR-S rubber) any desired concentration of double bonds can be obtained by controlling the amount of diene in the polymerisation mixture. The formation of unsaturated centres in polymers is not confined to polymerisation processes and many polymers undergoing degradation reactions develop either terminal or internal unsaturation. Examples of this are the formation of terminally unsaturated polymeric fragments from the thermal degradation of polyethylene[4] and from the radiolysis of polyisobutene,[5] and the development of conjugated double bonds in degraded polyvinyl chloride.[6]

The existence of unsaturated centres in polymers is of considerable importance since various types of reaction may be induced at these sites. Polymer chains can be joined together at the unsaturated bonds producing a cross-linked network. This reaction is of great commercial importance

and is termed vulcanisation in the rubber industry. A double bond also forms a centre at which another chain can be grafted to the polymer, and this has proved to be a useful method of modifying the physical and chemical properties of a polymer. The presence of double bonds may, however, be disadvantageous to the polymer with respect to thermal and chemical stability; they form points of weakness towards oxidative attack and may be active initiation centres for degradation reactions. In the study of such reactions it is desirable to be able to measure the number of double bonds present. There is also some interest in measuring very low unsaturations since the number of double bonds could be correlated with particular mechanisms of transfer or termination during polymerisation or possibly with the rate of initiation of degradation reactions.

METHODS OF MEASURING UNSATURATION.

The remarkable chemical reactivity of double bonds accounts for the great variety of analytical procedures which have been used to determine the unsaturation and many hundreds of papers in the literature have been devoted to the problem. The many methods of analysis have been reviewed by Polgar and Jungnickel[7] who classify the most

important analytical procedures as:-

Chemical: (a) Halogenation.

(b) Hydrogenation.

(c) Oxidation.

(d) Nitration.

Physical: (a) I.R. and U.V. spectroscopy.

(b) Polarography.

(c) Chromatography.

Many of these methods which have been used to estimate low molecular weight olefins have been employed either directly or with slight modification in polymer studies. The choice of method is usually restricted by factors such as the degree of unsaturation, the nature of the unsaturation, the specificity of the reagent, etc. A brief survey of some polymer applications is described below.

Halogenation methods:

Several halogenation techniques have been employed for the analysis of double bonds in commercial rubbers, e.g. butyl rubber.[8-12] In general, these methods consist of adding reagent, e.g., iodine, bromine, iodine monochloride, to a solution of the polymer and measuring the amount of reacted halogen by titration of the excess of reagent. The iodine chloride method of Lee, Kolthoff and Johnson,[9] and the iodine - mercuric acetate procedure of Gallo, Weise and

Nelson[12] gave satisfactory results for butyl rubber unsaturations, and the former method is still widely used for estimating double bonds. These methods work best for isolated double bonds and are unsatisfactory for systems possessing conjugated double bonds. Bromine vapour is a better reagent for this type of unsaturation and has been used by Thinius and Hagan[13] to measure polyene unsaturation in degraded poly (vinyl chloride). Another method, using the bromide-bromate reagent, has been successfully used to estimate double bonds in conjugation with ester groups as in acrylates.[14] None of the above reagents is universally applicable.

Hydrogenation methods.

Pepper and Reilly[15] have measured terminal unsaturation in oligomeric polystyrene using hydrogenation techniques. Apart from this, however, very little use has been made of the method in the measurement of polymer unsaturations. Nevertheless, analytical hydrogenation is applicable to all types of double bonds and has the advantage that errors due to substitution, which may occur in halogenation methods, do not arise. A micro-technique, using hydrogen generated in situ, has been described by Brown et.al.[16] This method could be adapted for the measurement of polymer unsaturations but the difficulty of accurately measuring the consumption of small amounts of hydrogen presents a

serious disadvantage.

Oxidation methods.

Rehner[17,18] reviewed several methods for determining unsaturations in butyl rubber and found that good results could be obtained using ozone as reagent. Unsaturations were estimated from the change in viscosity after ozonolysis or by analysis of the acidic end-groups produced by further treatment with hydrogen peroxide. The disadvantages of this method are that viscosity measurements are tedious and the method is destructive to the polymer. A second useful reagent in this class is perbenzoic acid; this reagent shows some selectivity towards different double bond structures and it has been possible to distinguish the internal and external double bonds in polybutadiene[19,20] owing to the faster rate of addition of the reagent to the internal bond.

Physical methods.

I.R. techniques have been commonly used for the qualitative identification of double bonds in polymers since certain structures e.g. $R_1R_2C{=}CH_2$ produce characteristic peaks in the I.R. spectrum. In some studies, quantitative data have been derived from the intensities of the absorptions. The unsaturation in polyethylene has been the subject of numerous investigations.[4,21-23] I.R. techniques have also proved amenable in elucidating the unsaturated

structures in natural and synthetic rubbers.[24-28]

MEASUREMENT OF LOW UNSATURATIONS.

The analytical procedures which have been outlined above are suitable for the measurement of relatively high unsaturations. In high polymers, however, the level of unsaturation may be so small that those methods become unreliable or even inapplicable. The minimum degree of unsaturation which can be accurately estimated is approximately 0.5 mole per cent, i.e. one double bond per 200 chain units. In order to measure lower unsaturations than this, it is necessary to use radiochemical techniques which are generally much more sensitive than chemical methods owing to the ease with which small amounts of a radioactive species can be measured. In theory, many of the conventional chemical methods could form the basis of a radiochemical technique; halogenating agents could be labelled with a suitable radioisotope, e.g. Iodine-131, Chlorine-36 and Bromine-82.

The two common halogenating reagents, iodine chloride and iodine-mercuric acetate, could be readily labelled with radioisotope but these reagents are not entirely satisfactory from a chemical viewpoint. The reaction between iodine chloride and a linear double bond, $R_1CH=CHR_2$, proceeds by the expected addition mechanism, but when the double bond

structure is branched, e.g. $R_1CH=C(R_2)CH_3$, a more complex mechanism is followed. Three stages can be distinguished:-

(1) Initial addition of ICl.

(2) Splitting out of HI which reacts with a second molecule of reagent to produce HCl and I_2.

(3) Slow addition of ICl to the double bond resulting from stage (2).

Despite this complexity, meaningful measurements can be made providing that the experimental conditions are carefully controlled. The iodine-mercuric acetate method suffers from a similar disadvantage; the mechanism of the addition is not well understood and in order to obtain reliable unsaturation values the empirical assumption is made that three iodine atoms are consumed per double bond.

From a radiochemical standpoint, chlorine-36 is by far the most attractive halogen isotope. It has a long half-life, 3.1×10^5 years, so that corrections do not have to be made for decay of the isotope during the analytical procedure. It is a pure B-particle emitter and can be detected using the relatively cheap Geiger-Muller counting equipment. Elaborate safety precautions are not necessary for the handling of radiochlorine since the radiation is of relatively low energy.

Because of these considerations, McNeill[29] developed a radiochemical technique using radiochlorine. This

technique was used to measure butyl rubber unsaturations but was potentially applicable to the estimation of much lower unsaturations. The use of chlorine in the past[30] has been very limited owing to the excessive reactivity of the reagent and the liklihood of side reactions. McNeill, however, devised a suitable experimental procedure in which undesirable reactions were obviated. Quantitative handling of the reagent was easily accomplished using vacuum apparatus. The extension of this method to the measurement of low unsaturations has been recently realised by Haider[31] and Makhdumi[32] who have investigated the unsaturation in polystyrene prepared by free radical and cationic mechanisms.

In the present study, the technique is applied to the determination of low unsaturations in polyisobutene which, as previously stated, was expected to exhibit terminal unsaturation. The first objective therefore was to test the sensitivity of the radiochemical technique; if a sample of polyisobutene had a number average molecular weight of 56,000 and each chain had one terminal double-bond, the degree of unsaturation would be 0.1 mole%. Hence, polyisobutene with molecular weights of this or higher values would provide a rigorous test for the technique. Since halogenating agents have been found to exhibit abnormal reactions with double bonds possessing substituents at the double bond, the mechanism of the chlorination was investigated

in order to obtain meaningful values of unsaturation from the chlorination data. A further facet of the work was to relate the measured unsaturations to those postulated from the theory of cationic polymerisation and to furnish quantitative evidence concerning the nature of the end-groups, which has evoked considerable discussion and speculation in the literature.[33,34]

DEGRADATION OF POLYMERS.

The rapid expansion of the plastics industry over the past twenty years has stimulated considerable industrial and academic interest in the degradation of polymers. Industrial emphasis is placed on the stabilisation of polymers and the development of new products which might show improved resistance to deterioration. In order to achieve these aims, a thorough understanding of the nature of degradation reactions is essential. The fundamental chemistry of these reactions has provided considerable scope to the pure chemist owing to the diversity of degradative behaviours exhibited by different macromolecular structures. The extensive investigations into the subject have resulted in the publication of a large number of papers and several monographs.[3,35-38]

The term 'degradation' describes any process which produces chemical modification in the polymer; chemical changes in the polymer structure are generally associated with a deterioration in the physical properties which make the polymer useful commercially. The most common agencies which are employed to promote degradation reactions are heat, light, high energy radiation and oxygen. Deterioration of commercial products is often induced by a combination of such agencies, but fundamental studies are usually restricted to reactions promoted by a single agency in order that the number of variables in the system may be minimised. In the work described in this thesis, heat was the only agency used so that further discussion is limited to thermal degradation reactions.

CLASSIFICATION OF DEGRADATION REACTIONS.[39]

Two types of degradation reactions can be distinguished in the thermal breakdown of polymer molecules:-

(a) Reactions which do not change the basic structural unit in the polymer chain. The products of such degradations consist of monomer units and/or chain fragments similar to the starting material in chemical structure.

(b) Reactions involving substituents in the polymer chain; these reactions produce changes in the chemical

nature of the repeating unit in the polymer by the modification of structural groups or the elimination of small molecules.

The reactions classified under (a) can be sub-divided into chain scission, or depolymerisation, reactions and cross-linking reactions.

(i) Depolymerisation reactions.

Two extremes of behaviour are shown in this group. The first type is illustrated by the degradation of polyethylene.[4] Examination of the degradation products for this polymer reveals a wide spectrum of chain fragments ranging from monomer to polymers containing approximately 70 methylene units. The formation of such products indicates that the scission of carbon-carbon bonds is completely random in polyethylene. The other extreme can be regarded as a reverse polymerisation in which degradation, once initiated, proceeds by an unzipping process to produce large amounts of monomer. Examples of this type of behaviour are provided by poly(methyl methacrylate)[40] and poly(α-methyl styrene).[41] Many polymers show intermediate degradation patterns in which appreciable amounts of both monomer and higher chain fragments are formed. Simha and Wall[42-44] have discussed these reactions in terms of a general, free-radical mechanism;

Initiation:- random $M_n \xrightarrow{k_i} P_j^{\bullet} + P_{n-j}^{\bullet}$

terminal $M_n \xrightarrow{k_i} P_{n-1}^{\bullet} + P_1^{\bullet}$

Depropagation:- $P_i^{\bullet} \xrightarrow{k_d} P_{i-1}^{\bullet} + M_1$

Transfer:- intermolecular $P_i^{\bullet} + M_n \xrightarrow{k_f} M_i + P_n^{\bullet}$

intramolecular $P_n^{\bullet} \xrightarrow{k_f} P_j^{\bullet} + M_{n-j}$

Termination:- $P_i^{\bullet} + P_j^{\bullet} \xrightarrow{k_t} M_i + M_j$ or M_{i+j}

In these equations, $P_i^{\bullet}$, $P_j^{\bullet}$, etc., and M_i, M_j, etc., represent respectively long chain radicals and dead polymer molecules of i,j, etc., monomer units in length. The above workers have treated the extremes of degradation behaviour theoretically. It has been since shown that these theories account reasonably well for the experimental results and kinetic curves.

The range of degradation patterns depends on variations in the relative importance of the above equations in different systems. It is generally possible to make some predictions concerning the degradation characteristics in terms of the structure of the polymer.[38] Thus 1:1 disubstituted polymers tend to undergo monomer-producing reactions since the primary radicals formed on initiation

are stabilised by the substituents and transfer reactions are suppressed owing to the absence of tertiary hydrogen atoms. The predominance of transfer reactions over depropagation reactions depends therefore on the availability of hydrogen atoms, preferably tertiary, and the reactivity of the primary radicals. Kinetic investigations of polymer systems are usually supplemented with molecular weight studies and with product analysis. Analysis of the products and the determination of monomer yields can often provide a useful qualitative picture of the degradation mechanism with respect to the relative importance of transfer and unzipping reactions. Similar information is derived from molecular weight studies which may also distinguish the two methods of initiation. The molecular weight of a polymer degrading by multiple random scissions falls very rapidly at the onset of degradation whereas that of a polymer which degrades by complete unzipping to monomer from the chain ends is maintained at its original value. By examining the rate of degradation as a function of the molecular weight the random and terminal initiations are readily distinguished. Random initiation is independent of chain length but terminal initiation is proportional to the number of chain-ends present.

(ii) Cross-linking reactions.

In this type of reaction long polymer chains are

joined together to form a three-dimensional network. This often leads to the development of insolubility in the degraded polymer and a characteristic rise in molecular weight would be observed. Cross-linking is achieved by the combination of pairs of radicals so that the phenomenon may constitute the termination step (page 15) of a degradation mechanism.

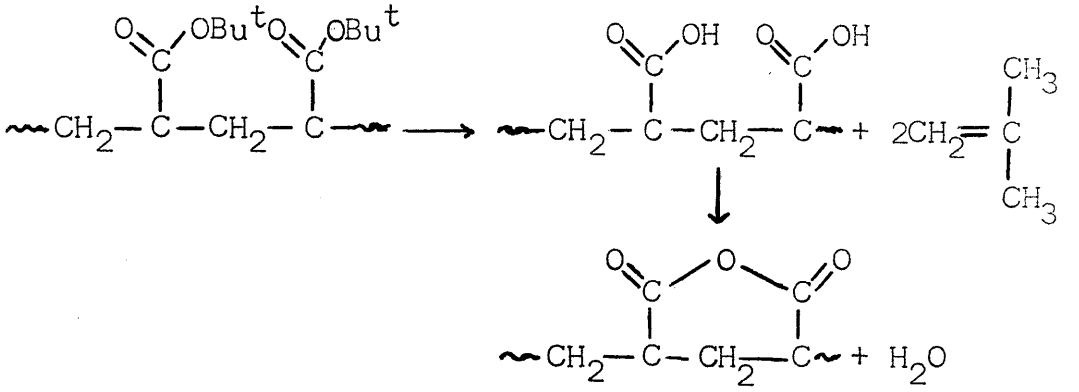
The substituent reactions can also be sub-divided:-

(i) Elimination reactions.

The thermal degradation of poly(vinyl chloride) provides a good example of this type of reaction. The extensive researches into the degradation of P.V.C. have been reviewed by Grassie;[39] the production of HCl can be explained qualitatively in terms of a free-radical process in which scission of a carbon-chlorine bond is followed by abstraction of a hydrogen atom. It is evident also that the HCl is liberated from adjacent units producing conjugated double bonds in the polymer backbone. The mechanism of initiation and the role of HCl in the degradation have been the subjects of considerable controversy.[45] Stromberg et.al. have suggested a free-radical mechanism involving scission of labile chlorine bonds in the polymer chain. More specific conclusions were deduced by Talamini and Pezzin[46] who, on the basis of the observed relationship between the rate of degradation and the molecular weight of the polymer,

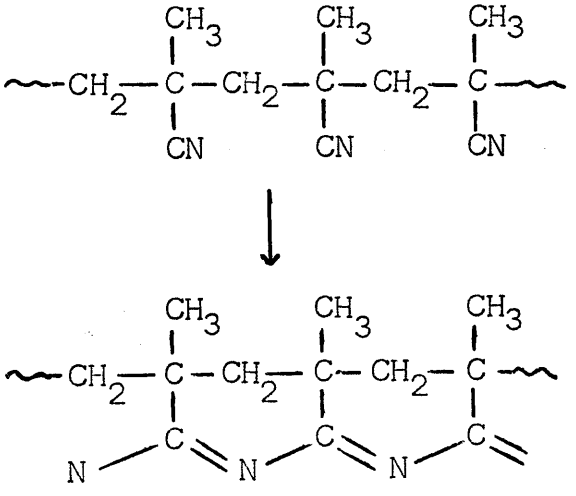
suggested that the weakest bonds in the polymer were those allylic to the terminal double bonds. In addition to chain-end initiation, Baum and Wartman[47] proposed that initiation might occur at branch points and impurity structures in the polymer chain. By reference to the degradation of chlorinated P.V.C., however, they concluded that the HCl loss in P.V.C. was primarily from unsaturated chain ends by allylic activation. The role of HCl has also been a topic of interest; it was believed by early investigators that HCl catalysed the reaction, but this has been refuted by Arlman[48] and Winkler.[49] Cross-linking reactions, which were defined in category (a) of this classification, can also occur in substituent reactions, and it has been suggested[45] that cross-linking occurs in the early stages of P.V.C. degradation.

Elimination reactions are exhibited by a number of polyesters such as poly(vinyl acetate)[50] and polymers of higher methacrylates. The reaction usually involves a cyclic, molecular mechanism by which a double bond is formed in the polymer and a molecule of acid is eliminated. Poly(tert-butyl methacrylate) provides an interesting variation.[51] In this case, the olefin is eliminated and the acid groups remaining in the polymer react further by anhydride formation, i.e.



(ii) Rearrangement reactions.

In this type of reaction substituents react with each other without elimination of small molecules. Nitrile polymers, e.g. polymethacrylonitrile,[52,53] are the best examples in this class; colour formation is observed in these polymers owing to the rearrangement of nitrile groups.



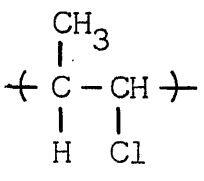
AIM OF PRESENT STUDIES.

The salient features of the degradation of polyisobutene and its relationship with respect to the above classification are well established, and are discussed in detail in Chapter 4. The motivation for studying the degradation of this polymer was two-fold. First, it was desirable to compare the results obtained by the pressure-method of analysis (see Chapter 2) to the data derived by previous workers.[38,54,55] Secondly, it was considered important to review the degradation behaviour of polyisobutene prior to studying the degradation of chlorinated polyisobutenes.

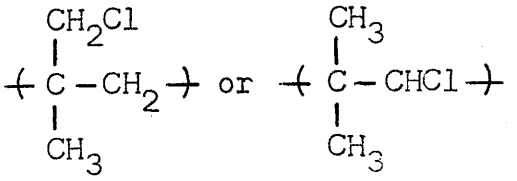
It was anticipated that the degradation of chlorinated polyisobutene would prove to be interesting with respect to the formation of HCl. The production of HCl in P.V.C. has been previously discussed. Other chlorinated polymers such as poly(vinylidene chloride) and chlorinated polypropylene also degrade by HCl formation. The degradation of poly(vinylidene chloride),[56] (P.V.D.C.), is similar to that of P.V.C. The thermal stability of P.V.D.C. is initially lower than that of P.V.C., HCl being rapidly evolved at temperatures exceeding 200°C. In P.V.D.C., however, the polymer is stabilised at 50% loss of chlorine since the residual chlorine atoms are vinyl to a double

bond. The stabilities of various P.V.C. and P.V.D.C. structures have been examined by Amagi and Murayama.[57] Although HCl is the main product of the degradation of chlorinated polypropylene,[58] the mechanism of the reaction is different from that in P.V.C. and P.V.D.C. In P.V.C. a free-radical mechanism operates but in chlorinated polypropylene an ionic mechanism for the HCl evolution has been postulated. The differences in mechanism are reflected in very different values of activation energy for the reaction, viz., 8k.cal./mole for chlorinated polypropylene and 24-36 k.cal./mole for P.V.C.[38,48]

In the degradation of chlorinated polyisobutene an important structural feature forbids the production of HCl by similar mechanisms to those described above; in polyisobutene it is impossible to have hydrogen and chlorine atoms on adjacent carbon atoms. The structures of chlorinated polypropylene and polyisobutene (1 H atom replaced) are represented by (A) and (B) respectively:-



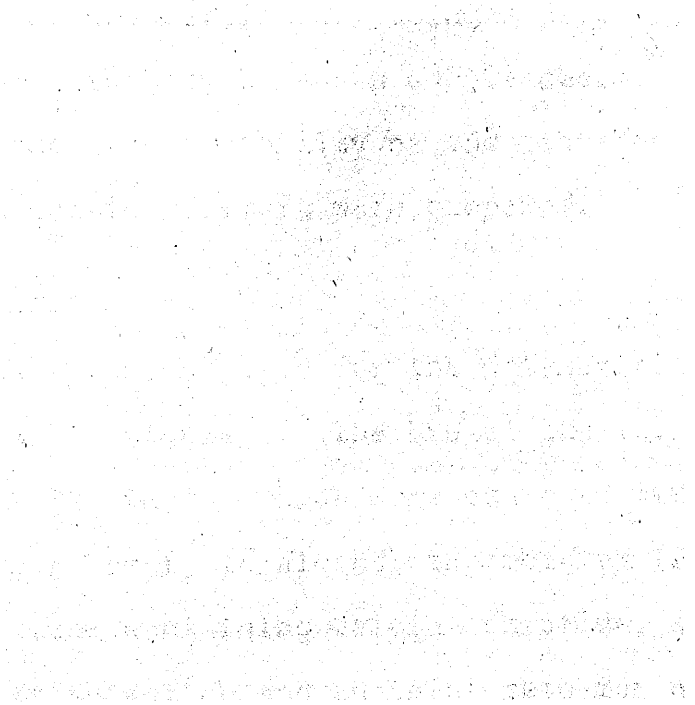
(A)



(B)

It is therefore of interest to observe whether

chlorinated polyisobutene does in fact produce HCl or whether the degradation proceeds by a different mechanism e.g. depolymerisation. The degradation behaviour of a series of polymers with different degrees of chlorine substitution is studied in Chapters 5 and 6.



CHAPTER 2.

APPARATUS AND EXPERIMENTAL TECHNIQUES.

SECTION 1. PREPARATION OF POLYMERS.

(i) THE PREPARATION OF POLYISOBUTENE.

The low-temperature, cationic polymerisation of isobutene was carried out using a procedure similar to that described by Sorensen and Campbell.[59] In order to check the reproducibility of the reaction conditions, four separate polymers were prepared.

Apparatus.

The apparatus used for the polymerisation of isobutene is shown in figure 1. The lid of the 1L. reaction vessel had six B19 inlets which were equipped with a monomer inlet tube, a stirrer, an alcohol thermometer ($20^{o}C$ to $-120^{o}C$), a drying tube containing calcium chloride, a serum cap for catalyst injection and an inlet tube for nitrogen.

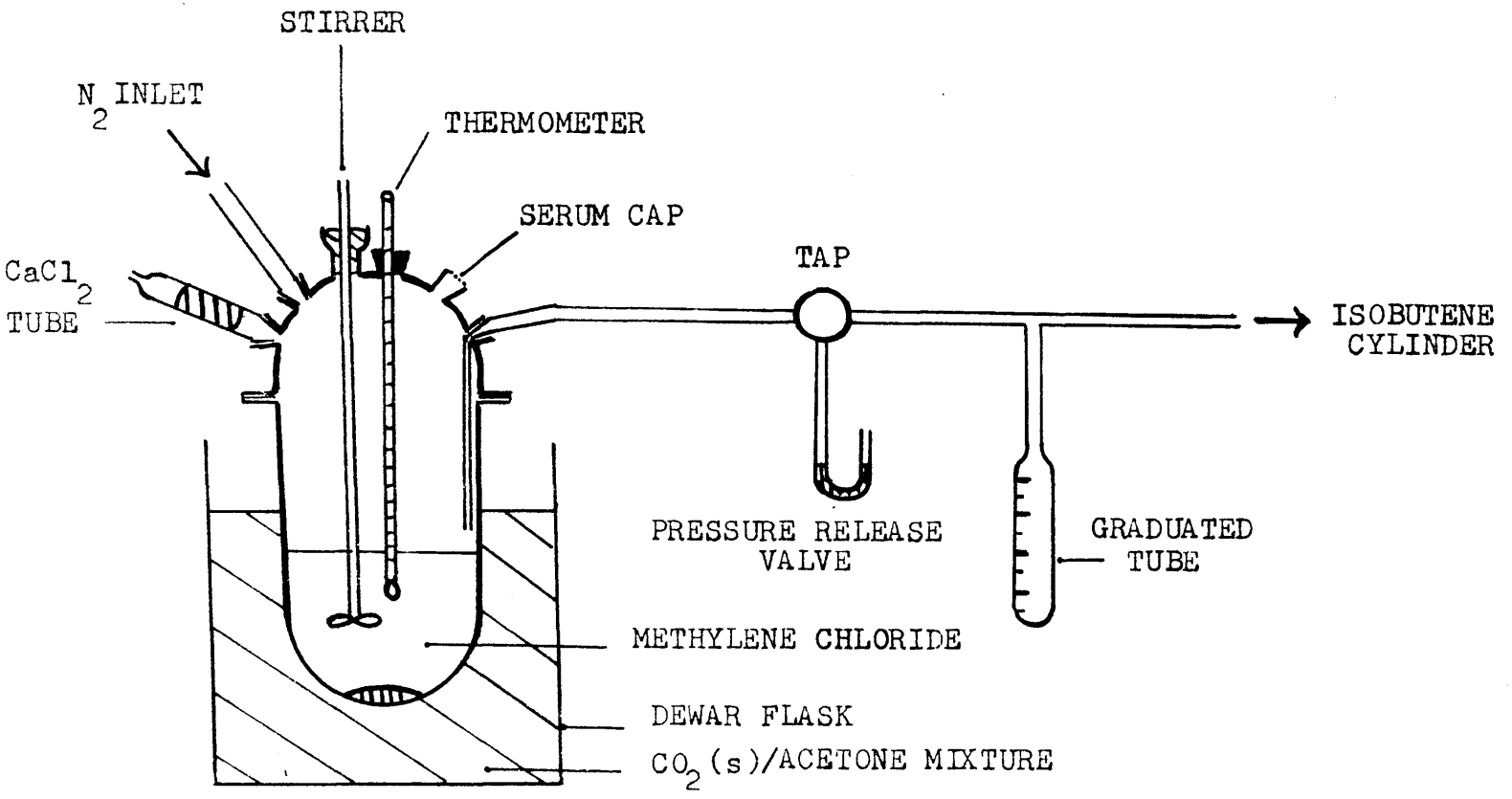


FIGURE 1. APPARATUS FOR THE POLYMERISATION OF ISOBUTENE.

Materials and quantities.

Isobutene (I.C.I. Ltd., Billingham)	- 50ml. at -190°C.
Methylene chloride (B.D.H. Ltd.)	- 450ml.
Calcium chloride, granular (B.D.H. Ltd.)	- 20g.
Stannic chloride (B.D.H. Ltd.)	- 0.5ml.

Procedure.

The reaction vessel was washed, rinsed with acetone and dried in an oven at 60°C. The requisite quantities of redistilled methylene chloride and calcium chloride were added. The purpose of the calcium chloride was to ensure a low, fairly reproducible water content in the vessel. Nitrogen was passed slowly into the vessel to provide an inert atmosphere above the solution, and the contents of the vessel were cooled to -78°C using a mixture of acetone and solid carbon dioxide. Isobutene was distilled from a cylinder into the 50ml. graduated flask and thence into the reaction vessel. The catalyst, stannic chloride, was introduced through the serum cap using a micro-syringe. As polymerisation proceeded, a slow rise in temperature, 1C° per 30 minutes, was observed and a sludge of polymer precipitated from the solution. The polymerisation was quenched with methanol (1L.) after three hours and the polymer purified by reprecipitation using n-hexane as solvent and ethanol (B.D.H. Ltd., absolute alcohol) as precipitant.

The polymers were dried by heating to 60°C in a vacuum oven for several days.

(ii) MOLECULAR WEIGHT MEASUREMENT.

The number-average molecular weights of the polymers were obtained from osmotic pressure measurements in toluene solution at 37°C. The instrument employed was a Mechrolab, Model 501, High Speed osmometer, the use of which has been described in detail.[60,61] Sylvania 300 grade gel cellophane membranes were normally used in the osmometer, but for low molecular weight samples, $\bar{M}_n < 40,000$, these were replaced by Ultracellafilter "allerfeinst" membranes (Membranfilter-Gesellschaft, Göttingen). From the measured osmotic pressures, plots were drawn of π/c versus C where π is the osmotic pressure and C the concentration in g.polymer per 100g.solvent. The intercept $(\pi/c)_o$ of the linear plot on the π/c axis, was inversely proportional to the molecular weight, $\bar{M}_n$. Thus,

$$\bar{M}_n = 2.63 \times 10^5/(\pi/c)_o \text{ at } 37^\circ C.$$

$$\bar{M}_n = 2.47 \times 10^5/(\pi/c)_o \text{ at } 20^\circ C.$$

The observed molecular weights for the prepared polyisobutenes are given in table 1.

TABLE 1. NUMBER-AVERAGE MOLECULAR WEIGHTS OF POLYISOBUTENE SAMPLES.

Sample	$(\pi/c)_o$	$\bar{M}_n$
IB1	5.75	45,700
IB2	5.35	49,100
IB3	6.40	41,100
IB4	2.63	100,000

(iii) FRACTIONATION OF POLYISOBUTENE.

A greater range of molecular weights was obtained by fractionating the highest molecular weight bulk polymer, IB4. This was achieved using a fractional precipitation technique[55,62] which consists of adding non-solvent to a solution of the polymer. A solution of 10g. polymer IB4 in 1L. AR benzene was prepared and AR acetone added slowly with stirring until a permanent turbidity was observed. The solution was heated until clear and allowed to cool slowly back to room temperature. The gel was separated and the polymer remaining in solution was precipitated using AR methanol. The gel was redissolved and the process repeated. Five fractions of approximately equal bulk were obtained in this way. The yields and molecular weights of

the fractions are given in table 2.

TABLE 2. MOLECULAR WEIGHTS OF FRACTIONATED IB4.

Fraction	Yield (grams)	M_n
F1	1.723	376,000
F2	2.665	190,000
F3	1.018	125,000
F4	1.633	77,000
F5	2.064	32,000

SECTION 2. CHLORINATION APPARATUS AND TECHNIQUES.

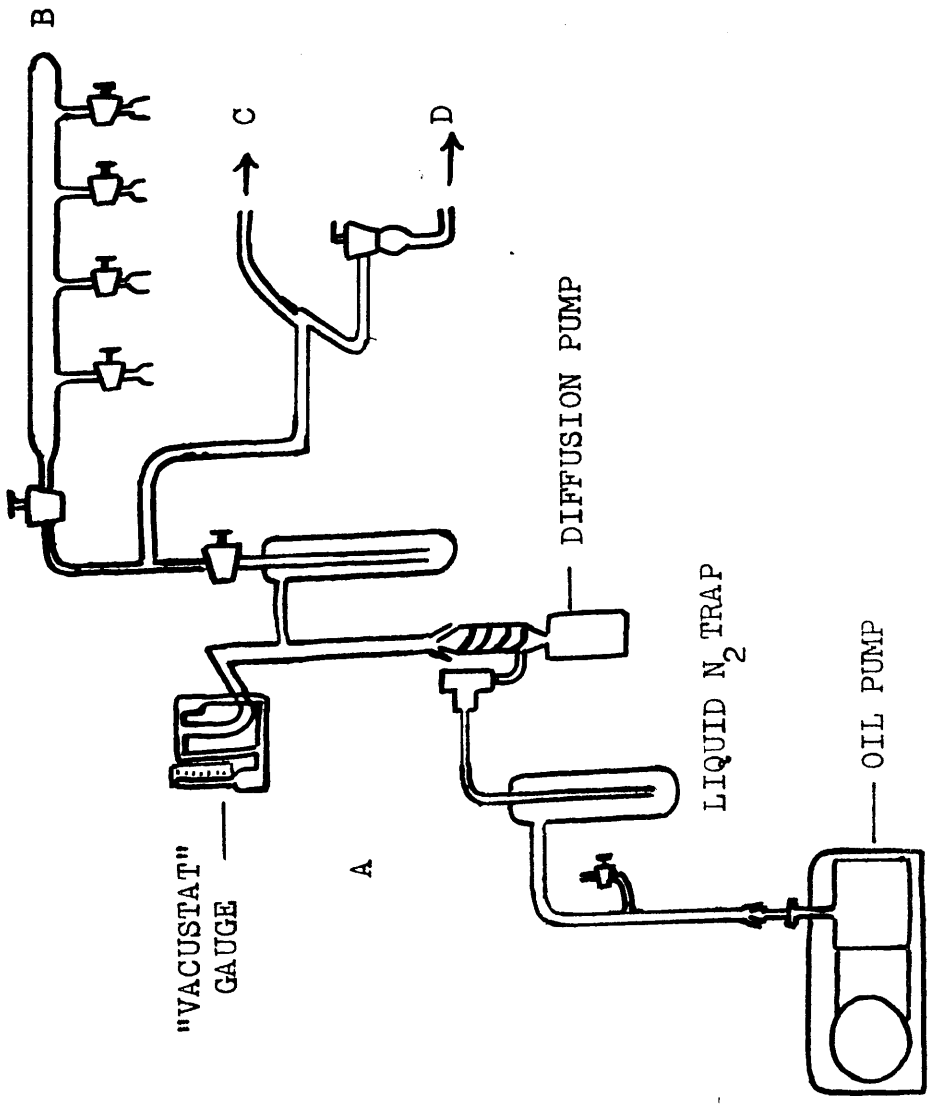
(i) VACUUM APPARATUS.

The vacuum apparatus had four distinct parts (figure 2).

(A). Pump Assembly:

Pumping was done by a gas ballast rotary pump (model 2Sc 20, Edwards High Vacuum Ltd.) and mercury diffusion pump (model 1M2B, Edwards High Vacuum Ltd.). Liquid nitrogen traps were used to remove condensable vapours present in the system. A "Vacustat" gauge (model 2G, Edwards High Vacuum Ltd.) was used for checking the vacuum. At best evacuation, the pressure was of the order 10^{-5} - 10^{-6} torr, and a

FIGURE 2. VACUUM APPARATUS.



"sticking" vacuum was observed in the gauge. Apiezon L grease was found to be satisfactory for all joints and taps except for those in the liquid nitrogen traps where silicone grease was used.

(B). General purpose manifold.

This part of the apparatus was used for the purification of volatile liquids by distillation and evaporation of solutions to dryness.

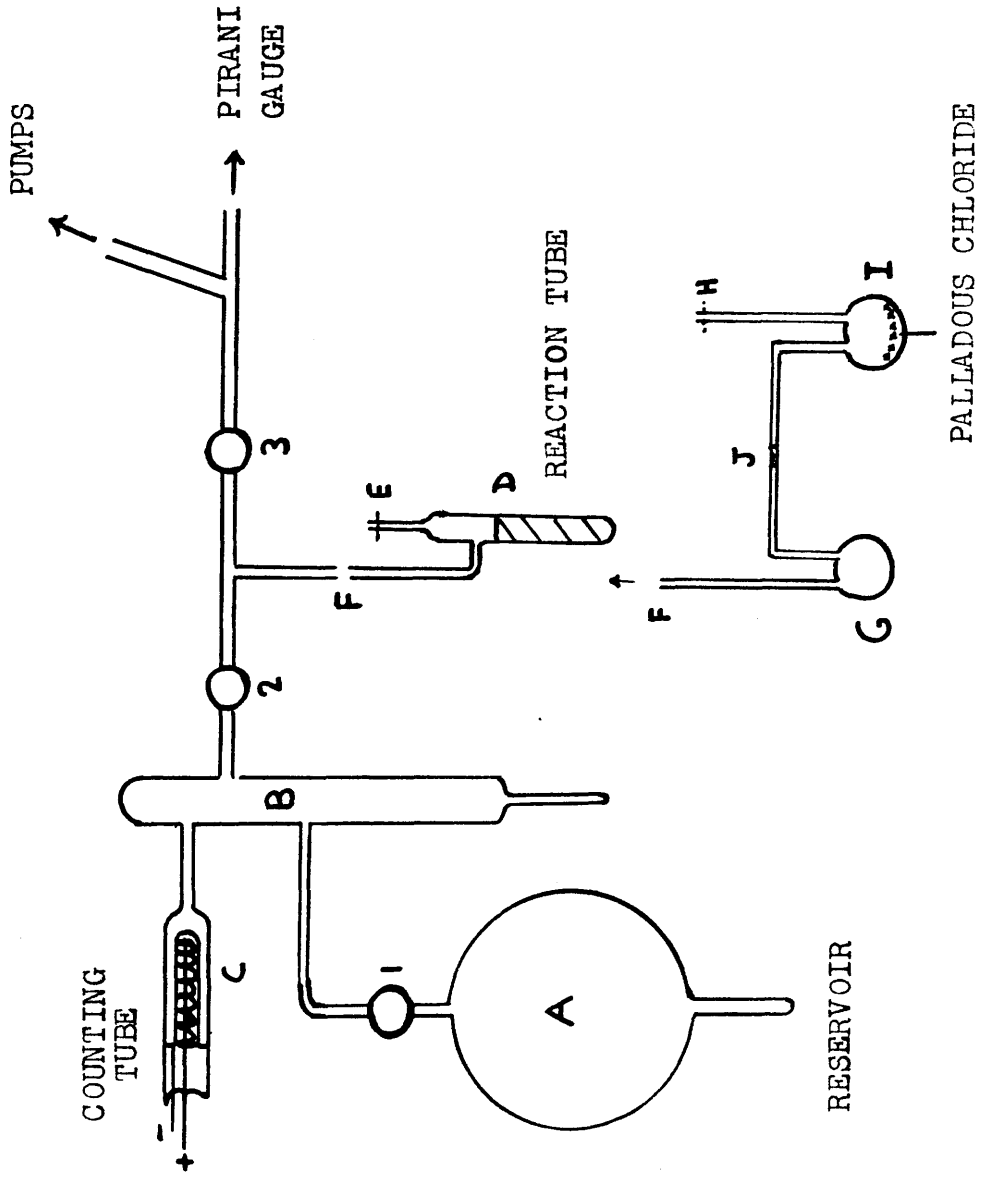
(C). Chlorination apparatus.

(D). Degradation apparatus.

(ii) CHLORINATION APPARATUS.

The apparatus used for the quantitative handling of radiochlorine is illustrated in figure 3. It was similar to that used by other workers in this field[29,31,32] but differed in the incorporation of a counting tube C (Mullard G.M.Tube, MX124) which was fused into section B. The volume of B was approximately one twelfth of the 3L reservoir A Stopcocks 1-3 were greaseless stopcocks (G.Springham and Co.Ltd.) with Viton A fluorocarbon diaphragms. The number of stopcocks was kept as small as possible since it was

FIGURE 3. CHLORINATION APPARATUS.



found that small splinters of glass from the reaction tube detachment point F gradually damaged adjacent stopcock diaphragms. When several stopcocks are together, it is not always obvious which is leaking.

(iii) PREPARATION OF RADIOCHLORINE.

The preparation of radiochlorine from labelled hydrochloric acid has been described by McNeill.[63] The hydrochloric acid, $H^{36}Cl$, (U.K.A.E.A.Radiochemical Centre, Amersham) was diluted to 100ml. and a specific activity of approximately 1μc/ml.60-120mg. palladous chloride (Baker Platinum Division, Engelhard Industries Ltd.) were placed in a r.b. flask and 10ml. of the hydrochloric acid solution added. The mixture was heated gently until the palladium salt had dissolved. The acid was carefully distilled off leaving labelled palladous chloride in the flask.

$$HCl^{*} + PdCl_2 \rightleftharpoons PdCl_2^{*} + HCl^{*}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{(reduced activity)}.$$

The flask was joined to another flask and the assembly, which is shown in figure 3 as a substitute for reaction tube D, attached to the chlorination apparatus at F. A plug of glass wool was inserted at J. The flask,I,was sealed at H. The flasks were evacuated, and the bulb,I,

heated gently to remove traces of moisture and acid. Vessel G was immersed in liquid nitrogen and bulb,I, heated with a large luminous flame, care being taken not to heat the bulb too strongly. The salt decomposed quantitatively to chlorine and palladium which formed a mirror-like deposit in the flask.

$$PdCl_2^* \xrightarrow{heat} Pd + Cl_2^*$$

The liberated chlorine was trapped in B before being transferred to the reservoir, A. The radiochlorine was usually diluted with ordinary chlorine to suit the needs of each series of experiments. This was done by passing chlorine (I.C.I.Ltd. Mond Division) into a flask or U-Tube of known volume, e.g. 100ml. and 500ml. as illustrated in figure 4. When the vessel was filled with chlorine at atmospheric pressure, it was sealed by closing the stopcocks, attached to the chlorination apparatus, and the chlorine distilled into the reservoir. The two flasks which were used gave 120mg. and 500mg. samples of chlorine which were mixed with the 40-80mg. of labelled chlorine.

(iv) CALIBRATION OF CHLORINE APPARATUS.

Transfer of known amounts of chlorine was accomplished by determining the volume ratio of the flask B to the total

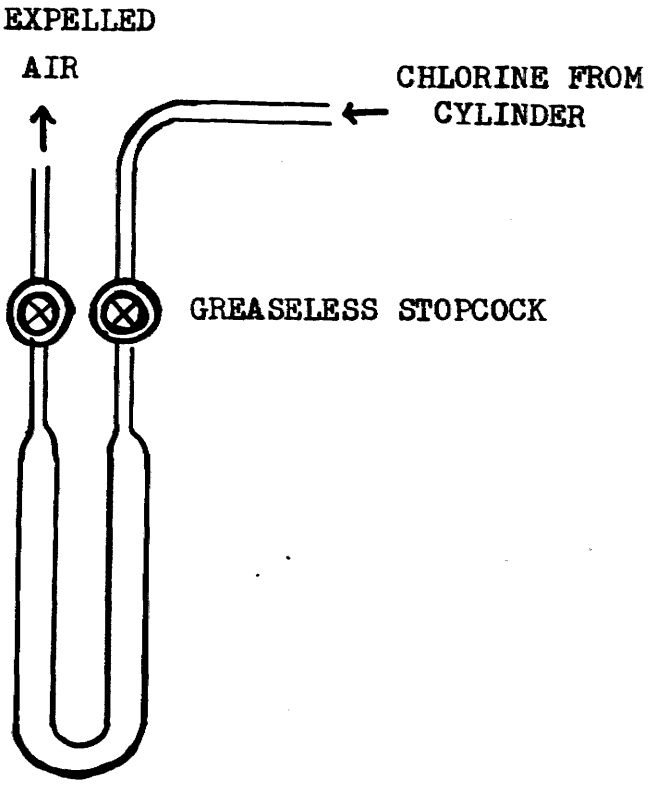


FIGURE 4. TRANSFER OF ORDINARY CHLORINE.

volume A+B. When the chlorine expands from A into A+B, the weight fraction W_B/W_{Total} is equal to the volume fraction B/A+B. This ratio is assigned the term "delivery fraction". Two methods of determining the delivery fraction are described below:

(a) Successive portions of chlorine were condensed into reaction tubes containing 10ml. of M/5 potassium iodide solution, which had been frozen in liquid nitrogen and evacuated. The reaction tubes were sealed off and allowed to thaw. The liberated iodine was estimated by titration against N/10 sodium thiosulphate solution (B.D.H.Ltd. volumetric reagent).

$$Cl_2^* + 2KI \longrightarrow 2KCl^* + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

1ml.N/10 thiosulphate $\equiv$ 3.55mg. chlorine.

The ratio of successive titres obeys the equation,

$$R = A/_{A+B} = 1-D$$

where D is the delivery fraction.

(b) The ratio R can be found radiochemically. Successive portions of chlorine obtained by expansion were counted using the counting tube C. The ratio of successive count

rates after correction (see Counting techniques) gave values of R. Results obtained by methods (a) and (b) are compared in table 3. The mean value of R was 0.932 so that the delivery fraction D = 0.068.

TABLE 3. DETERMINATION OF DELIVERY FRACTION.

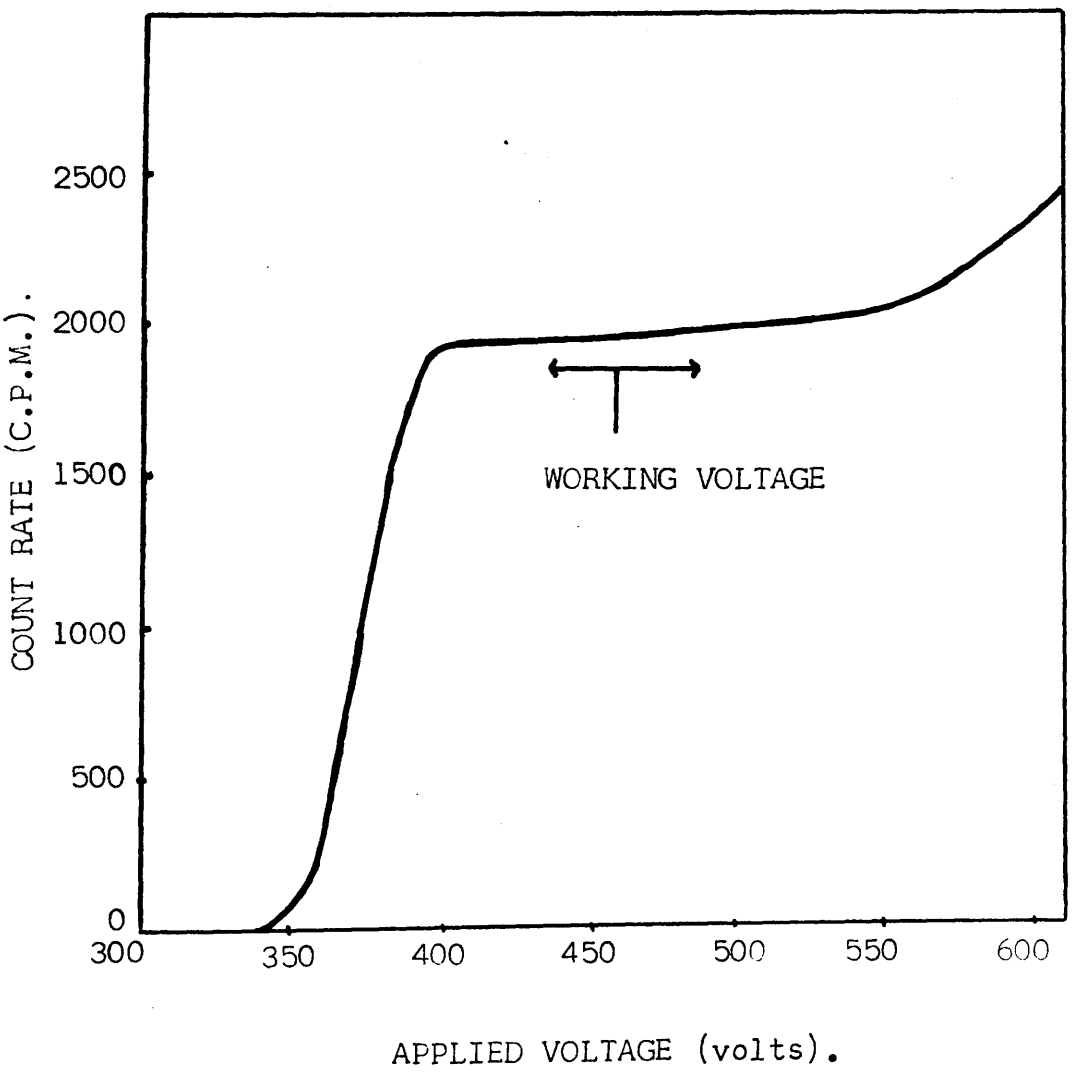
Fraction number (n)	Titre (ml.)	Corrected count-rate (c.p.m.)	Ratio (n/n-1)
1	2.270		———
2	2.115		0.932
3	1.940		0.917
4	1.820		0.938
5	1.710		0.939
6	1.590		0.930
7	1.475		0.929
8	1.355		0.919
9		7911	———
10		7452	0.942
11		6965	0.934
12		6408	0.920
13		6017	0.939
14		5627	0.935
15		5187	0.922
16		4838	0.932

(v) COUNTING TECHNIQUES.

Solutions were counted in open Geiger-Muller counting tubes (Mullard,MX 124) in conjunction with a G.M.scaling unit (type 121A, Ericsson Telephones Ltd.) and a probe unit (type 110A, Bendix-Ericsson Ltd.). Paralysis time was fixed at 400μs. and corrections for this dead-time in the instrument were made from published tables.[64] Chlorine gas was counted in the same type of tube, which was fused on to the chlorination apparatus as previously described. It is clear from table 3 that the count-rate in the tube is proportional to the total weight of chlorine in the vessel B.

Before using the counting tubes their plateau regions were determined by plotting the count-rate of a radioactive source against the applied voltage. A typical plot is shown in figure 5. For G.M.counting a voltage was selected corresponding to the mid-point of this plateau, i.e. 420-440v. All count-rates were corrected for paralysis time of the counter and background errors which were measured experimentally. Only the corrected count-rates are recorded in this thesis. With the exception of very slow count-rates, count-rates were measured by counting until 10,000 pulses had been registered. Time was measured by a stopwatch. Since the standard deviation on the count-rate is equal to the

FIGURE 5. DETERMINATION OF WORKING VOLTAGE FOR G.M.COUNTER.



square root of the total count,[64] the standard deviation of count-rates was ± 1%.

(vi) SPECIFIC ACTIVITY OF RADIOCHLORINE SUPPLY.

Before making use of the radiochlorine, the supply was characterised in terms of specific activity with respect to the two phases in which the chlorine was used. The specific activity in the gas phase, S.A.(G) was determined by counting a suitable fraction and condensing it into aqueous potassium iodide. The weight of chlorine was found as previously described. The specific activity is the count-rate (c.p.m.) divided by the weight (mg.). Knowing the value of SA(G) any desired quantity could be withdrawn from the reservoir and the weight of chlorine measured by counting. This method was extremely useful and was used in preference to the delivery fraction method.

The specific activity in carbon tetrachloride solution, $SA(CCl_4)$, was obtained by condensing a known weight of chlorine into a reaction tube containing a 5% solution of styrene in carbon tetrachloride. The solution was made up to a standard volume and a 10ml. portion counted in the G.M.tube. The specific activity in c.p.m/mg.Cl was calculated. The specific activity in other solvents, e.g. chloroform, was found by similar procedures.

It was found that the SA(G) and SA(CCl_4) values of any chlorine supply were related. The ratios, SA(CCl_4)/SA(G), observed for six chlorine supplies are shown in table 4. The average value, 2.83:1, was used to obtain the value of SA(CCl_4) from the SA(G) value of further chlorine supplies.

TABLE 4. COMPARISON OF SA(G) AND SA(CCl_4) VALUES.

	1	2	3	4	5	6
SA(G)	869	182	198	204	287	390
SA(CCl_4)	2500	517	563	570	814	1102
$\frac{SA(CCl_4)}{SA(G)}$	2.88	2.80	2.84	2.80	2.83	2.83

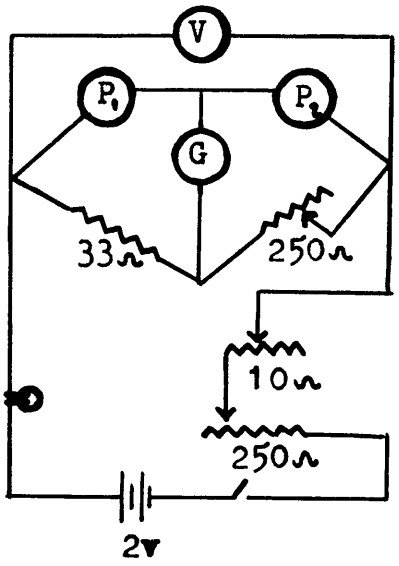
(vii) DETERMINATION OF UNSATURATION BY CHLORINATION.

250mg. samples of polyisobutene were dissolved in 10ml. AR carbon tetrachloride and the solutions transferred to reaction tubes attached to the chlorination apparatus (figure 3). The solutions were made up to 15ml., the tubes sealed at E, the solutions thoroughly degassed, and suitable amounts of chlorine transferred as previously described. The reaction tubes were sealed off at F and placed in a thermostat at 25°C for three hours. A dark

glass container was used to exclude light from the reaction mixtures. Chlorinations of other substances, e.g. model olefins, were performed in the same manner except that much smaller quantities of olefin were used.

Thorough degassing of solutions by repeated freezing, evacuation and thawing, was essential since it was found that side reaction could be promoted by traces of air in the reaction mixture. The degree of evacuation and degassing was followed using a pirani pressure gauge, the principle and use of which are well established.[65] The design used is shown in figure 6. In the circuit, P_1 was attached to the vacuum line and P_2 was a reference pirani which had been sealed off under vacuum. The gauges were immersed in a darkened thermostat to prevent spurious light and temperature effects. The measuring pirani was evacuated until a sticking vacuum was observed in the vacustat gauge. The voltage was adjusted to approximately 1 volt and the wheatstone bridge balanced using the variable resistances. Under these conditions the galvanometer deflection was zero, and any deterioration of the vacuum caused a deflection on the galvanometer. The pirani gauge provided a very sensitive check on the degree of degassing.

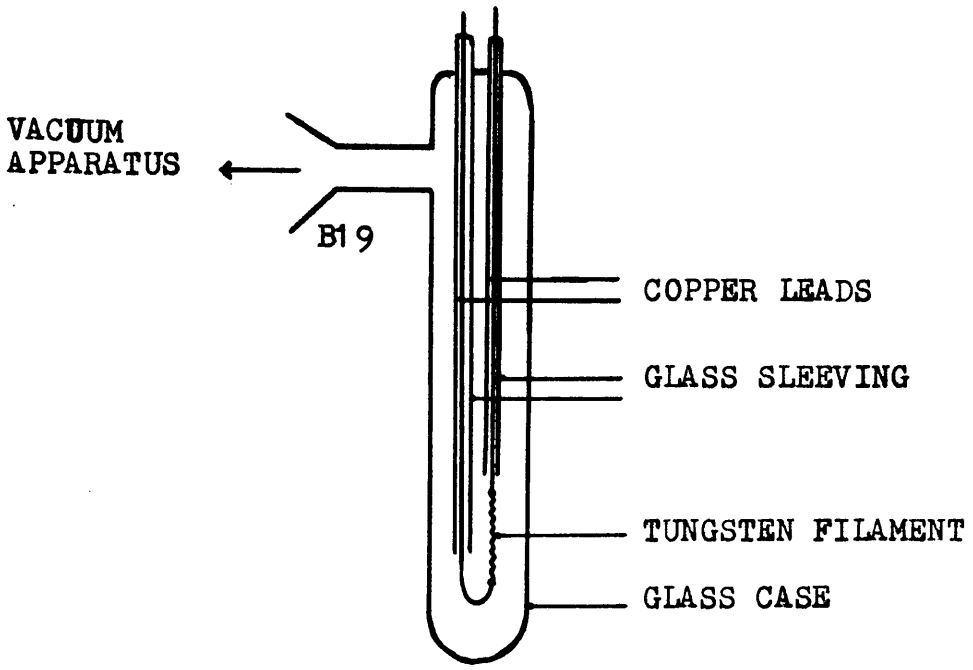
FIGURE 6. PIRANI GAUGE; DESIGN AND CIRCUIT.



V = VOLTMETER

G = GALVANOMETER

$P_{1,2}$ = PIRANI GAUGES



(viii) PURIFICATION OF REACTED SOLUTIONS.

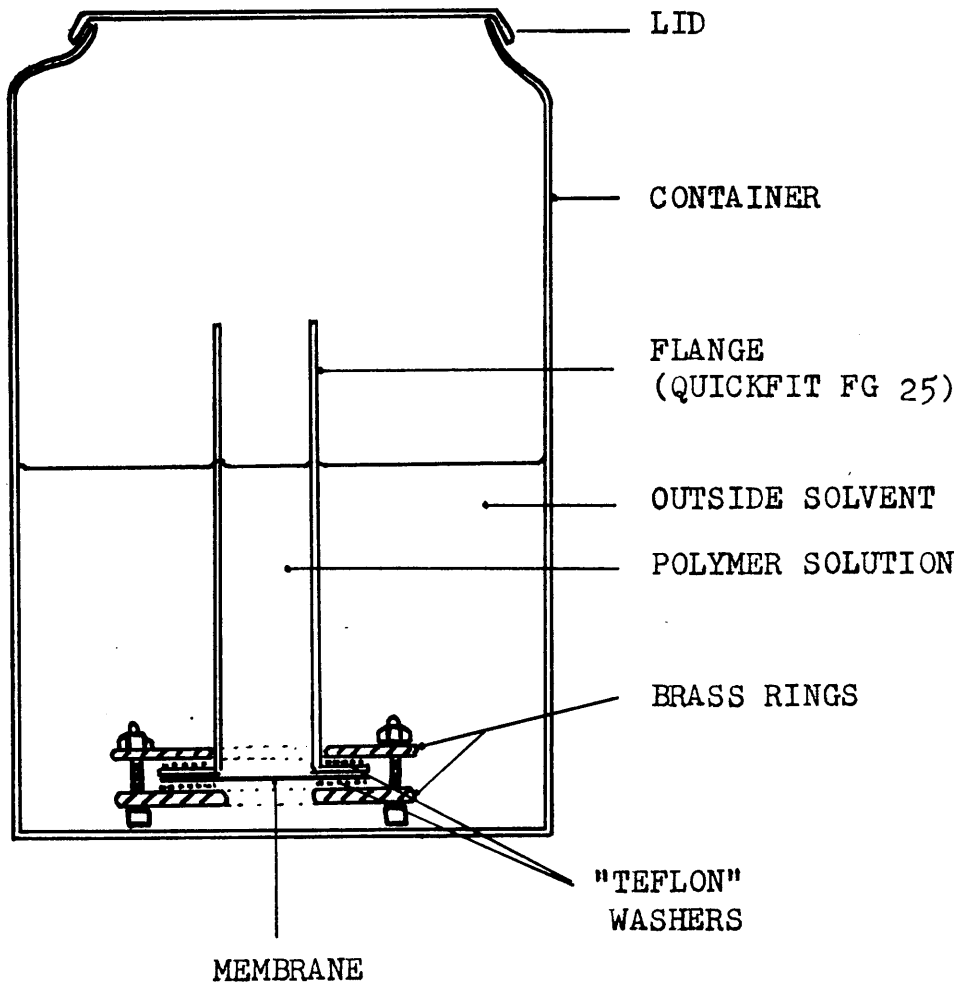
Immediately after reaction the solutions were treated to remove excess chlorine and products e.g. HCl. Three methods of purification were employed;

(a) The reacted polymer sample was precipitated in methanol and purified by reprecipitation. This method was not satisfactory for low molecular weight polyisobutenes which do not precipitate well. It was suspected that a crude fractionation would occur resulting in loss of low molecular weight polymer from the sample.

(b) The reaction products were shaken with an excess of aqueous sodium thiosulphate solution. The organic layer was separated, the extraction repeated twice, and the solution washed with water ten times. This method was used for studies of model olefins which could not be purified by methods (a) and (c).

(c) The most satisfactory method for purifying polyisobutene solutions was found to be dialysis. A diagram of the apparatus used is shown in figure 7. Reacted polymer solutions were first shaken with an excess of powdered sodium thiosulphate and filtered into the flange. Low molecular weight impurities can pass

FIGURE 7. APPARATUS FOR DIALYSIS OF POLYMER SOLUTIONS.



through the membrane but the polymer is retained. The membranes used were the same as those used in the osmometer and they were conditioned to carbon tetrachloride before being used.[66] The external solvent was renewed frequently and dialysis was continued until a constant count-rate was observed for the polymer solution. Since this took between ten and fourteen days, the dialysis time was standardised at fourteen days. By keeping the solvent and solution levels the same, solvent transfer to the flange was avoided.

When dialysis was complete, a 10ml. portion of the purified solution was counted and the chlorine content calculated from the specific activity, $SA(CCl_4)$.

(ix) PREPARATION OF MAIN-CHAIN CHLORINATED POLYISOBUTENES.

Chlorinations of the polyisobutene chain were carried out using the same apparatus as before. A wide range of chlorine-polymer ratios was selected in order to prepare polymers with different degrees of chlorination. Reaction vessels of 25,50 and 100ml. capacity were used depending on the amounts of chlorine and polymer which were required. The flask was attached to the chlorination apparatus and

a carbon tetrachloride solution of the polymer IB4 added such that the reaction flask was about half-full. The flask was sealed, the solution thoroughly degassed, and the predetermined weight of chlorine condensed into the flask. The flask was carefully sealed off and placed in a thermostat at 60°C for three hours. The addition of free-radical initiators, e.g. azobisisobutyronitrile, was found to be unnecessary and did not increase markedly the extent of chlorination. It is probable that reaction was complete within 30 minutes of immersion in the thermostat since it was observed that the green colour of solutions with high initial chlorine contents disappeared within this period. The chlorinated products were purified by reprecipitation and dried at 60°C in a vacuum oven. The degree of substitution was determined radiochemically using the $SA(CCl_4)$ value of the chlorine supply.

SECTION 3 DEGRADATION APPARATUS AND TECHNIQUES.

(i) GLASS APPARATUS.

The apparatus constructed for degradative work is shown in figure 8. Its position in the vacuum assembly is shown in figure 2 (D). Tubing was of a fairly wide bore, 10-15 mm, in order to assist rapid evacuation. The degradation tube A and the adjacent section B were constructed from FG 35 Quickfit flanges. B was equipped with B19 sockets for pirani gauge and thermocouple insertion. Taps 1-5 were 10 mm single pump stopcocks (G.Springham and Co.Ltd.). Sections D and E were designed for preliminary trapping of volatile degradation products.

(ii) HEATING SYSTEMS:

(a) ISOTHERMAL DEGRADATION.

For isothermal work the heater consisted of a heating mantle of 100ml. capacity (model MB, Electrothermal Eng. Ltd.) which was controlled by a "Transitrol" unit (Ether Ltd.) by means of a copper-constantan thermocouple placed in the mantle. An external thermocouple was necessary for precise termperature control and measurement.

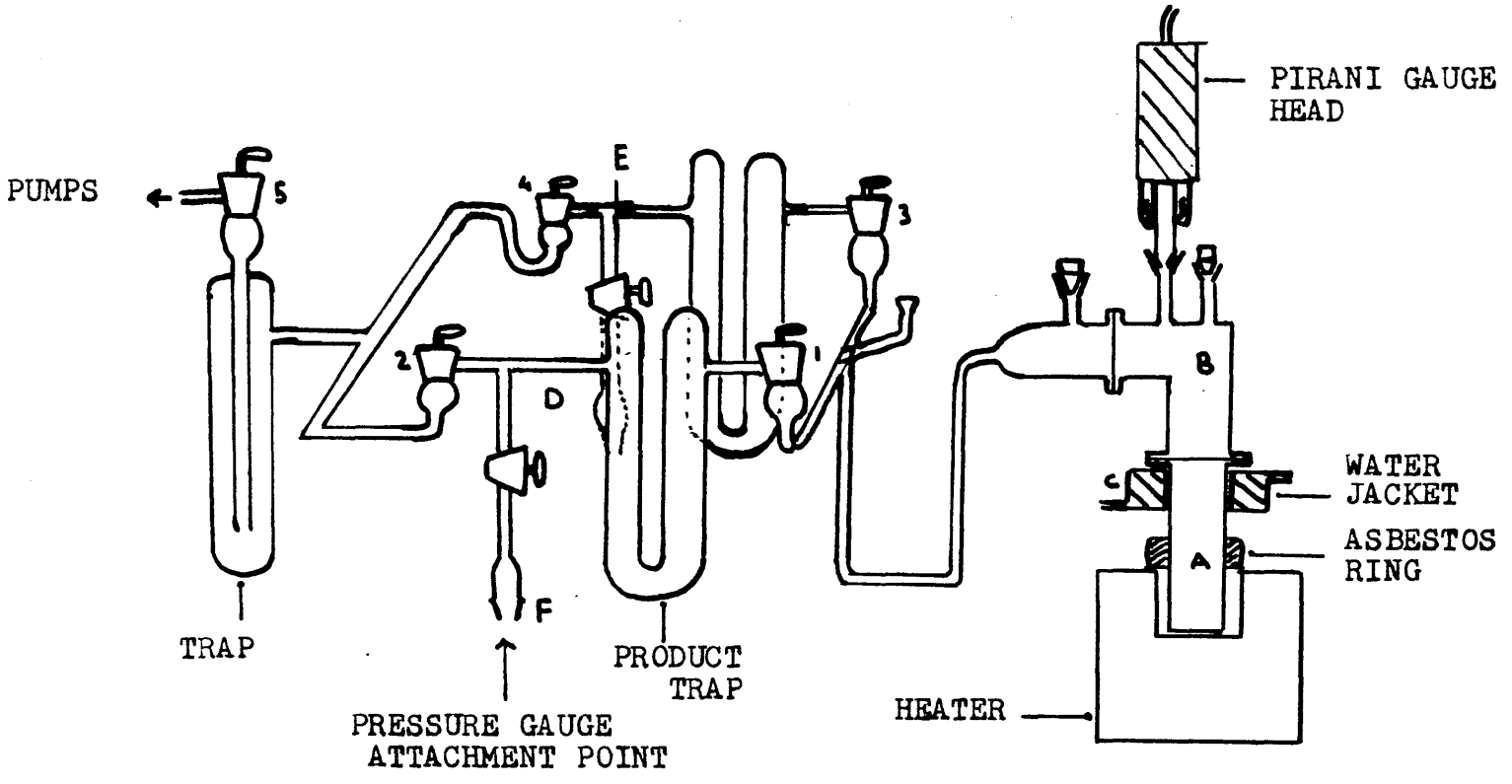


FIGURE 8. DEGRADATION APPARATUS.

Several thermocouple arrangements were investigated with thermocouples placed inside and outside the degradation tube but reproducible calibration could not be obtained. In order to achieve reliable temperature control it was decided to fuse a thermocouple into the base of the degradation tube. Copper-constantan thermocouples were not suitable for this purpose since the metals did not fuse to glass, the junction was too bulky to be inserted into the thin glass bottom of the tube and the thermocouple tended to oxidise at high temperatures. A thermocouple was constructed therefore from platinum and platinum-13% rhodium, (Johnson, Matthey and Co.Ltd.). The hot and cold junctions were made by spot-welding 6" lengths of the two wires together and copper wire was used to complete the circuit. The platinum thermocouple required a more sensitive voltmeter than a copper-constantan thermocouple and a thermocouple potentiometer (Derritron Instruments Ltd.) was used for accurate measurement of the E.M.F. In order to calibrate the constructed thermocouple, the hot junction was bound to the bulb of an immersion thermometer and inserted into an oven capable of giving a range of temperatures from room temperature to 500^{o}C (see Section 3 (ii) B). The E.M.F. of the thermocouple corresponding to various thermometer temperatures in the above range was noted and a graph constructed by plotting the

temperature against the thermocouple E.M.F. The experimental curve was identical to that constructed from published data[67] (figure 9) and it was concluded that the thermocouple behaved as a thermocouple made completely from platinum and platinum/rhodium providing that the copper junctions were not subjected to any temperature differential. A diagram illustrating the thermocouple arrangement is shown in figure 10.

Heating of the degradation tube was investigated for various "Transitrol" settings in the range 100-400°C. It was found that the rate of heating was very fast, the temperature of the tube lagging behind the mantle temperature. This is illustrated in figure 11, which shows the rise in temperature of the mantle and degradation tube for a "Transitrol" setting of 350°. At equilibrium, the platinum thermocouple exhibited a small temperature fluctuation, $\pm$1C°, which was related to the thermostatting action of the "Transitrol" unit.

Since the tip of the hot junction was very close to the inside surface of the degradation tube, it was expected that the temperature of a polymer sample being degraded would be very close to that recorded by the thermocouple. This was tested in a series of experiments using small pieces of metals with melting points in the range 200-350°C. The metals were heated on a film of Apiezon L

FIGURE 9. TEMPERATURE - E.M.F. RELATIONSHIP FOR PLATINUM - PLATINUM/RHODIUM THERMOCOUPLE.

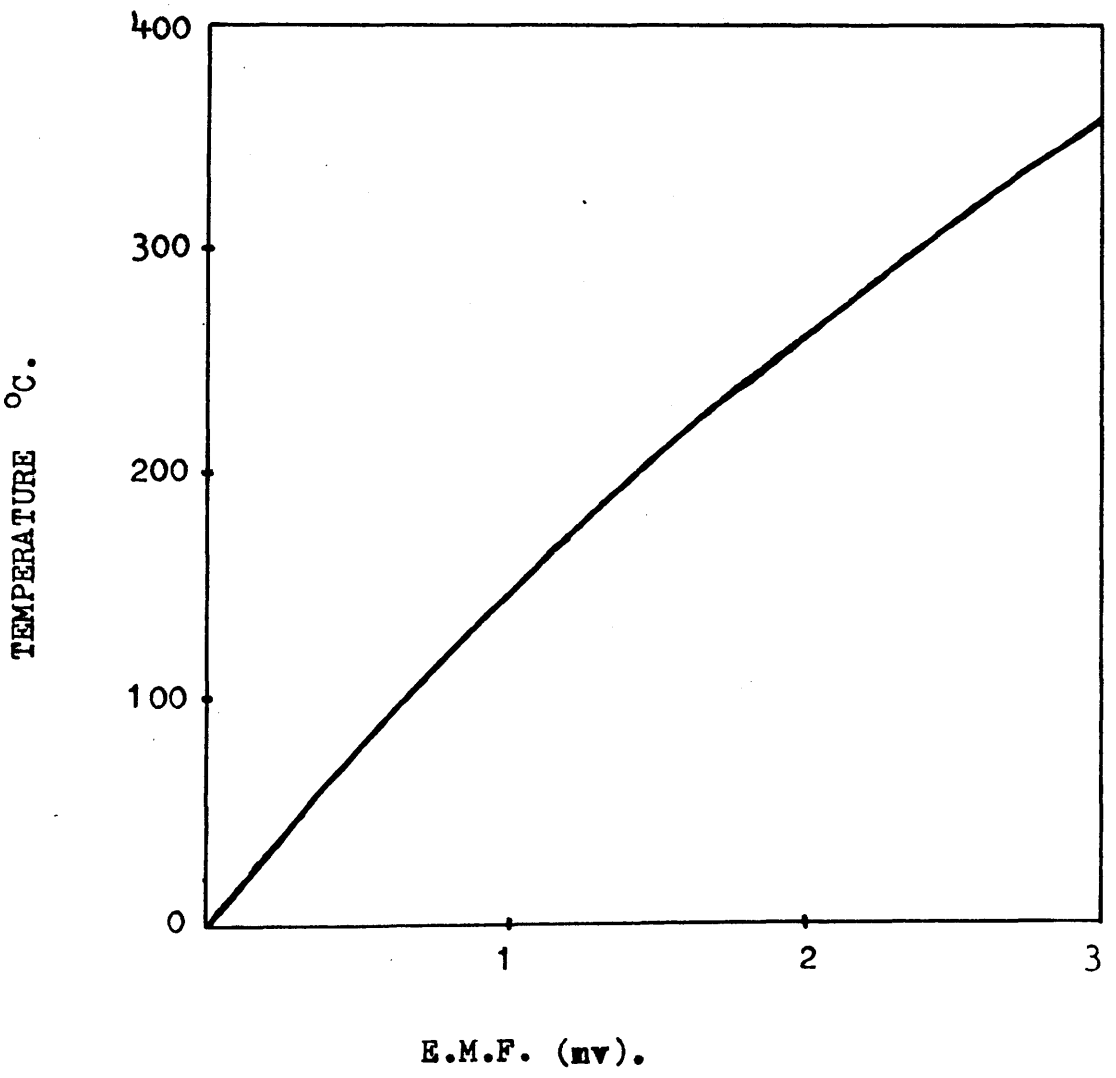
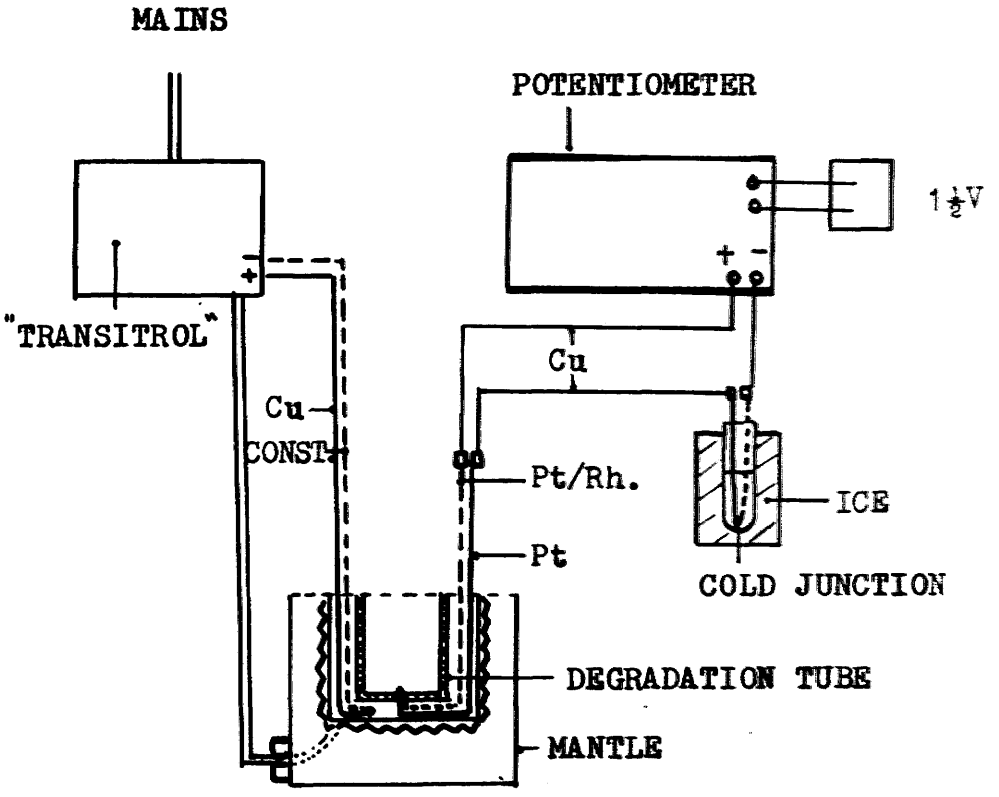


FIGURE 10. MANTLE AND THERMOCOUPLE CIRCUITS.



grease which was used to simulate a polymer sample during degradation. The temperature of the tube was raised by small increments using the "Transitrol" control and the physical appearance of the metals examined after each adjustment. The results of two series of experiments are summarised in Table 5. The data show that the internal temperature is near to that indicated by the thermocouple. The metals melted within a few degrees of the thermocouple reading the melting point temperature, and in some cases the events were coincident. The agreement was independent of the degree of evacuation, experiments being carried out at atmospheric pressure, low vacuum (0.05 torr) and high vacuum (10^{-4} torr). It was concluded that the thermocouple was satisfactory for measuring the temperature of degradation.

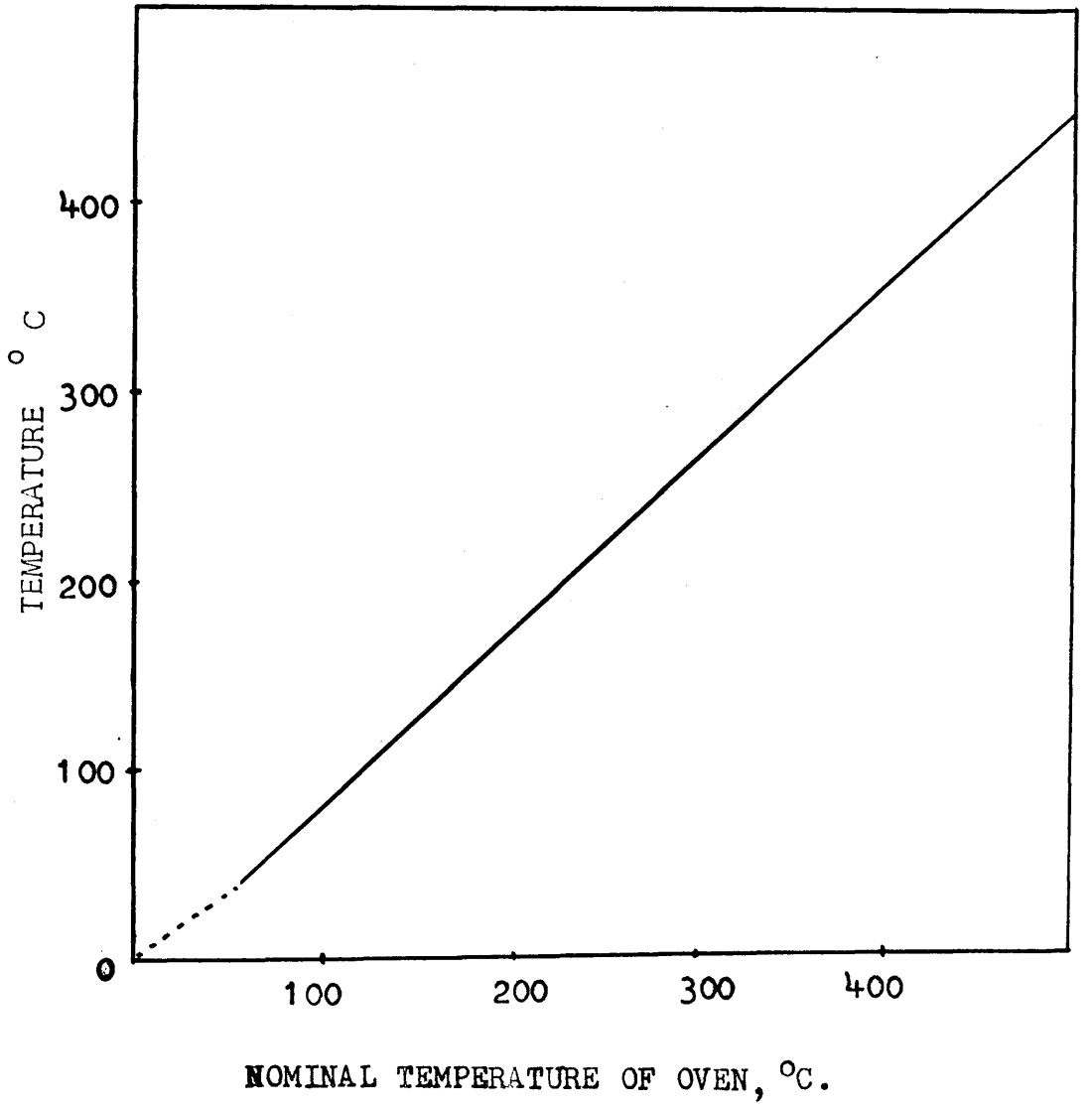
(b) TEMPERATURE-PROGRAMMED DEGRADATION.

The heater consisted of a precision oven (Perkin Elmer Ltd. Model F.11) with a linear temperature programming unit. A circular hole was cut in the roof of the oven so that three inches of the degradation tube could be immersed in the oven. A calibration curve was constructed relating the internal temperature of the tube to the nominal temperatures of the programming unit for the set rate of heating.[68] This is shown in figure 12. The internal

TABLE 5 RESULTS OF TEMPERATURE CALIBRATION EXPERIMENTS USING PIECES OF TIN, M.P. = 232°C, BISMUTH, M.P. = 271°C, AND LEAD, M.P. = 327°C.

Vacuum	"Transitrol"	Pt. thermocouple		State of metals		
	°C	mv.	°C	Tin	Bismuth	Lead
	220	1.73	227	solid		
	223	1.76	231	melting		
	225	1.79	234	molten		
	265	2.13	271		solid	
LOW	267	2.14	272		melting	
(0.05 torr)	270	2.16	274		molten	
	320	2.61	321			solid
	323	2.66	325			solid
	325	2.69	329			molten
	223	1.72	226	solid		
	225	1.73	227	melting		
	228	1.74	228	melting		
	230	1.79	234	molten		
	265	2.10	267		solid	
HIGH	268	2.12	270		melting	
(10^{-4} torr)	270	2.13	271		melting	
	272	2.14	272		molten	
	275	2.15	273		molten	
	327	2.64	324			solid
	330	2.68	328			molten

FIGURE 12. TEMPERATURE CALIBRATION FOR TEMPERATURE - PROGRAMMED DEGRADATION.



temperature was measured by a copper-constantan thermocouple, the hot junction of which was immersed in "Apiezon" grease and pressed firmly against the base of the tube.

(iii) PRESSURE MEASUREMENT USING PIRANI GAUGE.

Pressure changes during degradation were measured by a pirani gauge head (type G5C2) in conjunction with a pirani gauge control (model 8/2, Edwards High Vacuum,Ltd.). This gauge is a commercial version of the type of gauge previously discussed (page 41) and works on the same principle. The model used had two pressure ranges;

(a) Low pressure:- 10^{-4} - 5 x 10^{-3} torr.

(b) High pressure:- 5 x 10^{-3} - 1 torr.

Calibration of pirani gauge.

The pirani was attached to the degradation apparatus close to the degradation tube (figure 8). The apparatus was evacuated and all traps immersed in liquid nitrogen. When the best vacuum was attained the gauge was adjusted so that it read 10^{-4} torr (zero) on the low pressure scale. The pirani was calibrated using isobutene gas, in order to convert pirani readings into true pressures and rates of isobutene transfer.

(a) Relationship between Gauge pressure and true pressure.

The pirani unit, as supplied by the manufacturer and installed as described in the instruction manual (D.I.217/6), is calibrated to read directly the pressure of dry air. The meter does not register the true pressure of other gases since the response of the instrument depends both on the number of gas molecules and the thermal conductivity of the gas. The pressure recorded on the meter of the gauge was compared to the true pressure of isobutene using the apparatus shown in figure 13. The operation of the manometric pressure gauge is described in Section 3 (iv). The pressure gauge and the expansion flask Q were evacuated and a sample of isobutene gas condensed into P. Its pressure was measured in mm. of mercury using a cathetometer (The Precision Tool Co.Ltd.). The gas was expanded into the volume P+Q and from the change in pressure in the gauge an expansion ratio was obtained. The greaseless stopcock, S, was closed and the isobutene pumped from Q. The residual isobutene in A was again expanded into P+Q. The process was repeated until the pressure of gas in Q could be measured by the pirani gauge. The true pressures calculated from the original manometric measurement were compared with the pirani pressures. The relationship which is shown in figure 14, was linear over much of the pressure range examined but deviated at both extremes.

FIGURE 13. APPARATUS FOR PIRANI GAUGE CALIBRATION.

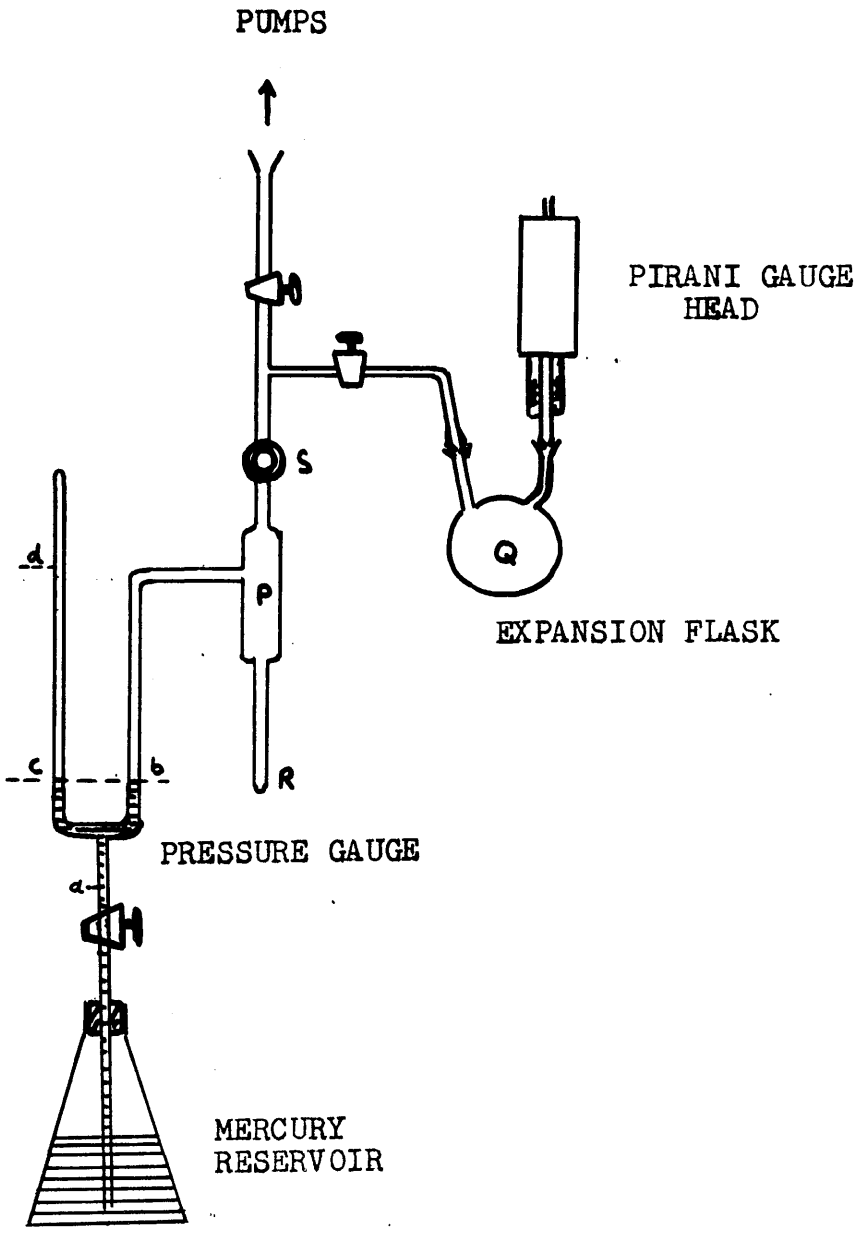
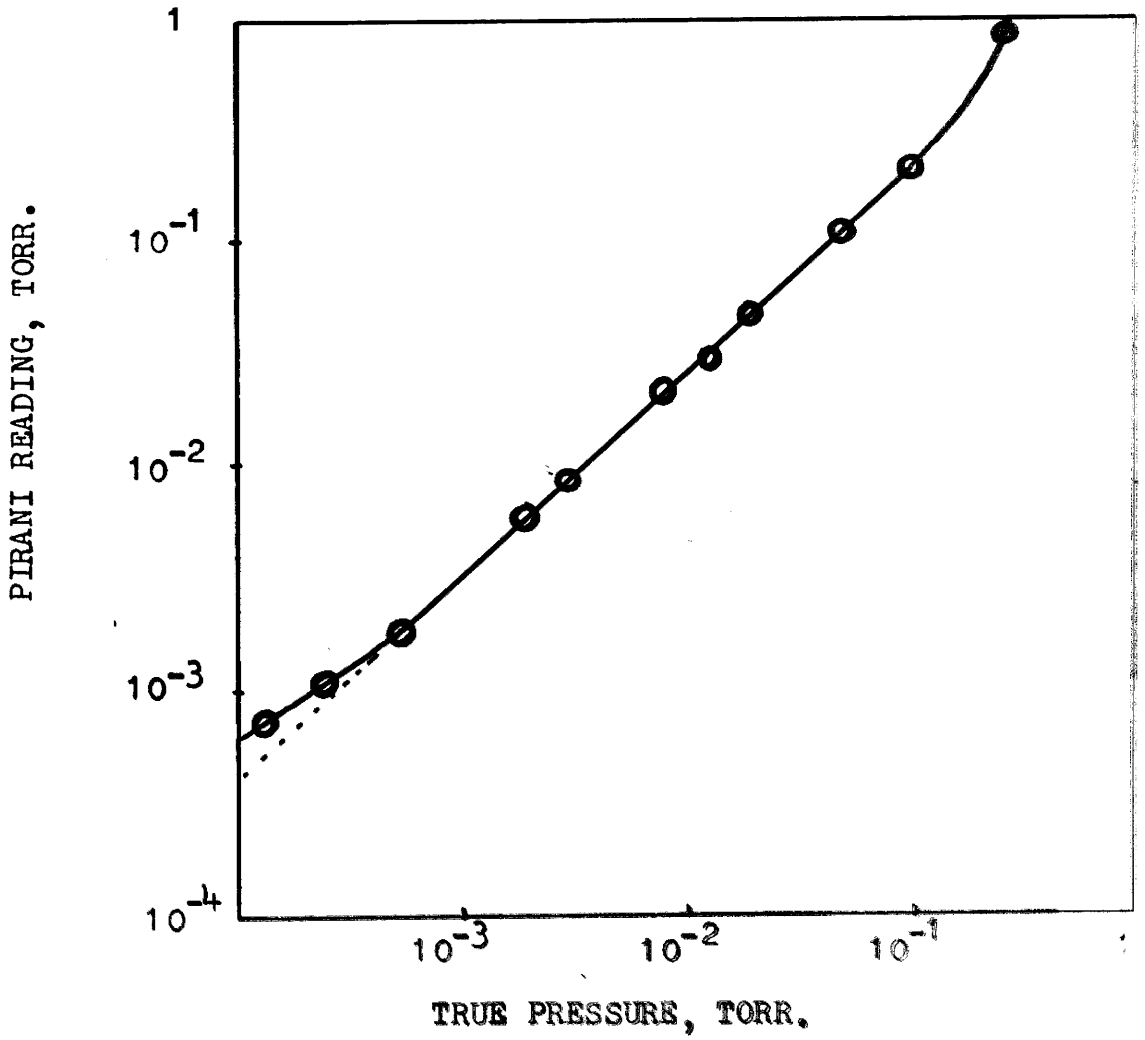


FIGURE 14. PIRANI CALIBRATION FOR ISOBUTENE.



The deviation at low pressures was probably experimental. Experiments of this nature indicated that the true pressure was lower than the pirani pressure by up to one power of ten.

(b) Pirani pressure and rate of flow of isobutene.

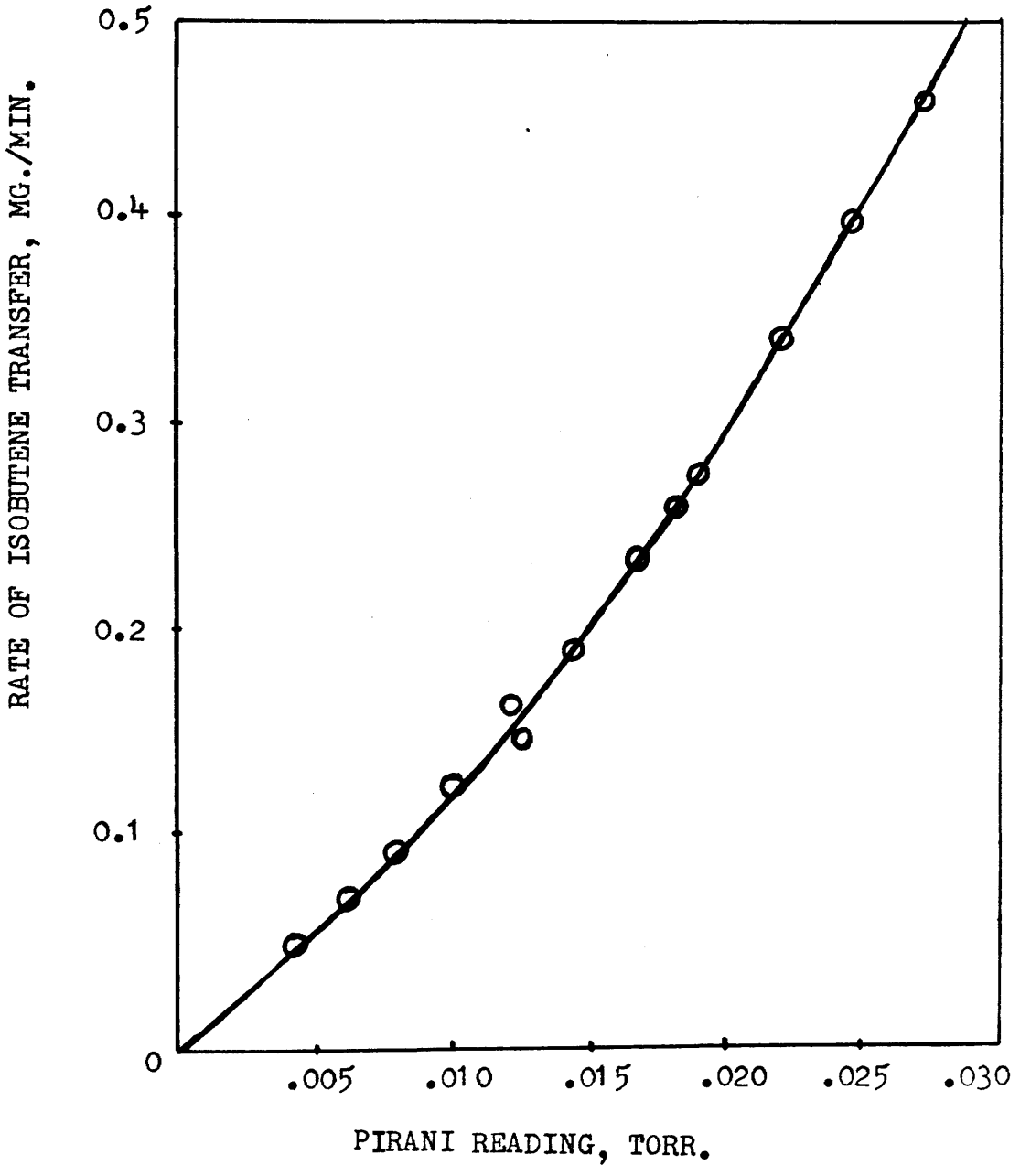
The degradation apparatus was assembled as if for degradation except that a needle value (Edwards High Vacuum Ltd.) was inserted beside the pirani gauge. Isobutene was passed into the apparatus via the valve and the valve adjusted to give a steady pirani reading. The isobutene was trapped in the product trap and after a suitable period had elapsed, the weight of trapped isobutene was measured either directly by distilling into a weighing tube or indirectly by using the pressure gauge. The results are shown in figure 15 as a graph of rate of transfer of isobutene versus pirani pressure (meter reading).

(iv) DEGRADATION TECHNIQUE.

(a) Temperature-programmed degradations.

For this type of degradation, the pirani gauge was linked to a recorder ('Speedomax' H, Leeds and Northrup Ltd.) so that automatic traces of pirani voltage against time were obtained. Recorded voltages could be converted

FIGURE 15. RELATIONSHIP BETWEEN PIRANI READING AND RATE OF ISOBUTENE TRANSFER.



to pressures using the conversion table given in the pirani gauge instruction manual. A heating rate of 10^{o} per minute was used and nominal oven temperatures, e.g. $100^{o}C$, $200^{o}C$, etc., were marked on the trace. The sensitivity of the recorder was varied to suit the size of polymer sample, e.g. 10mv. f.s.d for a 25 mg.sample, 1mv. f.s.d for a 5mg. sample. Samples were degraded as small pieces or powders depending on the physical form of the starting material.

(b). Isothermal degradation.

In isothermal work accurately weighed samples of the order of 40-100mg. were used. Highly chlorinated polyisobutenes were introduced as a layer of fine powder. Polymers which could not be readily powdered were evenly distributed in the degradation tube in the form of films cast from n-hexane or chloroform solution. As the degree of chlorination of polyisobutene increases, the product becomes less soluble in solvents, such as hexane, carbon tetrachloride and toluene, and only chloroform was suitable as a solvent. Special film-making procedures were not adopted; the sample was dissolved in approximately 2ml. of solvent in the degradation tube and the solvent allowed to evaporate overnight. All polymers were molten at degradation temperatures so that both forms of sampling gave a thin film of molten polymer during degradation.

The removal of all traces of solvent prior to degradation was essential. This was done by evacuating the degradation apparatus and heating the sample to 100°C. The preheating process was continued for 1 hour or until the pirani gauge indicated that the best vacuum had been reached. The product trap D (figure 8) was now cooled in liquid nitrogen and the temperature setting raised to the degradation temperature. Heating of the mantle took two to three minutes and the temperature of the tube was followed using the platinum thermocouple. The exact degradation temperature was obtained by making slight adjustments to the "Transitrol" setting. Zero time was taken as the moment the thermocouple indicated that the temperature of degradation had been reached. The pressure reading on the pirani gauge was observed at various time intervals; for isothermal work, the gauge was not linked to a recorder and meter readings were taken visually.

Rates of degradation.

A qualitative picture of the rate of volatile production was obtained from pirani measurements. For polyisobutene degradations the pirani readings were converted into quantitative results using a calibration curve which was derived from the isobutene calibration (figure 15) by correcting for the difference in weight for equal pressures of isobutene and degradation volatiles.

This is described further in the following section and in Chapter 4 (page 129). Supplementary information was derived by the following procedure: at various times of degradation, the flow of volatile products was altered from route D to route E (figure 8) by manipulation of stopcocks 1-4. The products which were isolated in trap D were distilled into a measuring device, e.g. pressure gauge, which was attached at F. The flow of products was then returned to the original pathway and the process repeated. A cumulative picture of the formation of volatile products was obtained.

Manometer type pressure gauge.

This gauge has been mentioned briefly in relation to pirani calibration and forms part of figure 13. The gauge operates on the general gas law principle,

$$PV = nRT \qquad .....(1)$$

where P is the pressure, V the volume, n the number of moles of gas, R the gas constant and T the temperature. For the simplest case of one species being present,

$$P(\text{observed}) = \left(\frac{RT}{MV}\right)w = kw \qquad .....(2)$$

where w is the weight of gas and M the molecular weight of the species.

In practice, the gauge was used as follows. The gauge was attached to the vacuum line and mercury allowed to

enter the gauge up to level (a). The gauge was completely evacuated and the mercury level raised to levels (b) and (c) in each limb so that the closed limb was isolated from the volume P. Volatile products were distilled into finger R by cooling R and heating the product trap D in the degradation apparatus. With tap S closed, the cold finger was heated to room temperature and as the pressure of volatiles forced the mercury down from (b) and up from (c) more mercury was allowed to enter the gauge from the reservoir so that the mercury level at (b) was maintained. As a result, the volume occupied by the volatiles remained constant and the pressure was measured as the difference in levels, (d) - (c), using the cathetometer. Before using the gauge for degradation experiments its accuracy was checked for isobutene. The volume, P, of the gauge was determined by filling the gauge with mercury up to level (b) and measuring the amount of water required to fill the remaining volume. A sample of isobutene was condensed into the gauge and its pressure measured. The weight was calculated using equation 2 above. The gas was then distilled into an evacuated collection tube (see figure 16) which could be detached from the apparatus and weighed on a balance. The good agreement between the two methods of weight determination is shown by the results presented in table 6. A relationship was similarly

derived between the pressure of volatile products from polyisobutene degradation and their total weight. This assumed that the composition of products remained constant during degradation. The pressure of volatiles at various times of degradation was expressed as a percentage of the pressure observed for 100% volatilisation of the sample. This gave the % volatilisation and the data was equivalent to that obtained by weight loss. This supported the assumption that the product distribution remained approximately constant during degradation. From the % volatilisation and pressure data it was possible to construct graphs of rate of volatilisation versus time or % volatilisation.

TABLE 6. VERIFICATION OF GAS LAW FOR PRESSURE GAUGE.

Volume of gauge (ml.)	Temperature (^{o}C)	Measured Pressure (cm)	Weight of Sample from Eq.2 (mg.)	Weight using balance (mg.)
54.8	22	12.605	21.0	21.6
54.8	24	9.560	15.9	16.1

Counting device for rate measurement.

The volatile products derived from degradation of chlorinated polyisobutenes were studied by measuring the chlorine content by counting. The apparatus which is shown in figure 16 replaced the pressure gauge. The counter was calibrated by relating the specific activity, SA', of the degradation counter to the specific activity, S.A.(G), of the chlorine supply used to make the chlorinated polymer. This was done by isolating a sample of radioactive products in the counting chamber, measuring the count-rate, c.p.m.', and transferring the volatiles to the original chlorination apparatus. The new count-rate, c.p.m. was measured so that,

$$\frac{SA'}{SA(G)} = \frac{c.p.m.'}{c.p.m.}$$

Using the value of SA' for each polymer count-rates were converted to weights of chlorine present in the volatiles and graphs constructed showing the build-up of chlorine with respect to time of degradation.

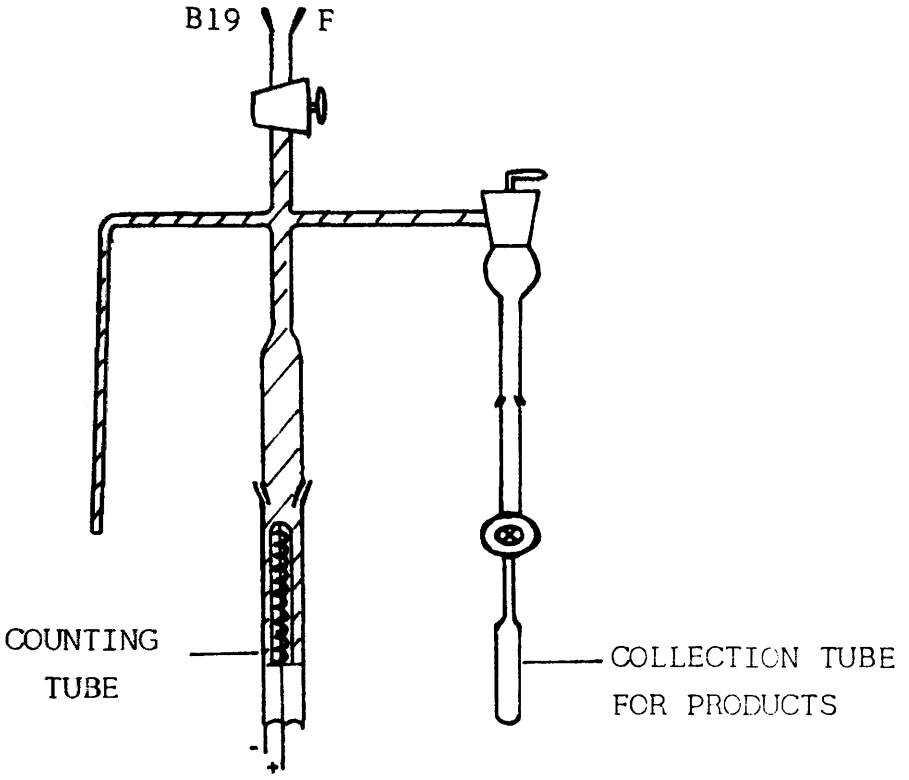


FIGURE 16. COUNTING APPARATUS FOR RADIOACTIVE DEGRADATION PRODUCTS; SHADED AREA DENOTES VOLUME OCCUPIED BY VOLATILES DURING COUNTING.

SECTION 4. ANALYTICAL PROCEDURES.

(i) STRUCTURE OF POLYMERS.

Infra-Red Spectra.

I.R. spectra provided qualitative information about the structure of polymers and degradation residues. Polymers were examined as 10% solutions in carbon tetrachloride. Where this was not possible other solvents, e.g. chloroform, were used and in some cases potassium chloride disc techniques were employed. Spectra were obtained using either a Perkin-Elmer, model 237, double beam spectrophotometer or a Unicam spectrometer, model SP 100, with a SP 130 grating.

P.M.R. Spectroscopy.

Proton magnetic resonance spectra were used for structural studies of chlorinated polyisobutenes and degradation residues. Samples weighing approximately 50mg. were examined in the solution state using carbon tetrachloride or deuterated chloroform, $CDCl_3$, as solvents. The instrument used was a Perkin-Elmer R.10 60Mc/s spectrometer with integrator.

(ii) VOLATILE PRODUCTS OF DEGRADATION.

HCl analysis.

The gaseous HCl was condensed into 2ml. of water and the resulting solution titrated against standard N/10 sodium hydroxide using screened methyl orange as indicator. Since only small quantities of base were required for neutralisation, the volume of NaOH was measured using a 2ml. microburette. It was checked that the results obtained by this method were in good agreement with those obtained by titration against standard silver nitrate solution with fluorescein as indicator. Since this reagent is specific for chloride ions, it was concluded that HCl was the only acidic species in the solution.

G.L.C.Analysis.

A Perkin-Elmer model 451 fractometer was used for investigation of hydrocarbon products of degradation. Samples were collected from the degradation apparatus in gas-tight tubes (figure 16) and introduced into the fractometer using a Hamilton gas-tight syringe. Golay capillary columns with "Carbowax" (polyethylene glycol) or Apiezon L grease as stationary phase were usually employed. Separations were carried out at temperatures in the range 20-60^{o}C with helium as carrier gas, and

the eluted components were detected using a flame ionisation detector.

Mass spectrometry.

An A.E.I.-MS9 mass spectrometer was used to obtain mass spectra of the gaseous products. The samples were collected in gas-tight tubes, with B14 outlets, which were attached to the spectrometer inlet system.

Combined G.L.C. - Mass spectrometry.

An L.K.B., model 9000A, gas chromatograph-mass spectrometry unit was used. Samples were again introduced in the gaseous state. In this instrument the mixture was resolved in a "Reoplex" (polyethylene glycol adipate on Embacel) column and the eluted compnnents analysed by the mass spectrometer.

CHAPTER 3.

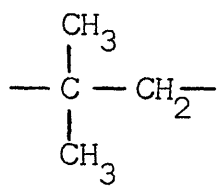
MEASUREMENT OF UNSATURATION BY RADIOCHLORINE METHOD.

INTRODUCTION.

The measurement of unsaturation by various techniques has been discussed in Chapter 1. It was pointed out by McNeill[29] that, because of their inherent sensitivity, radiochemical methods could be used to determine unsaturations outwith the scope of conventional techniques. The tracer technique has recently been used by Makhdumi[32] and Haider[31] to investigate low unsaturations in polystyrene. In this chapter, the measurement of low unsaturation in polyisobutene is examined in detail and the nature of the chlorination reaction discussed with respect to experimental results obtained for substances of known unsaturation and information derived from the studies by other investigators of reactions between chlorine and olefins.

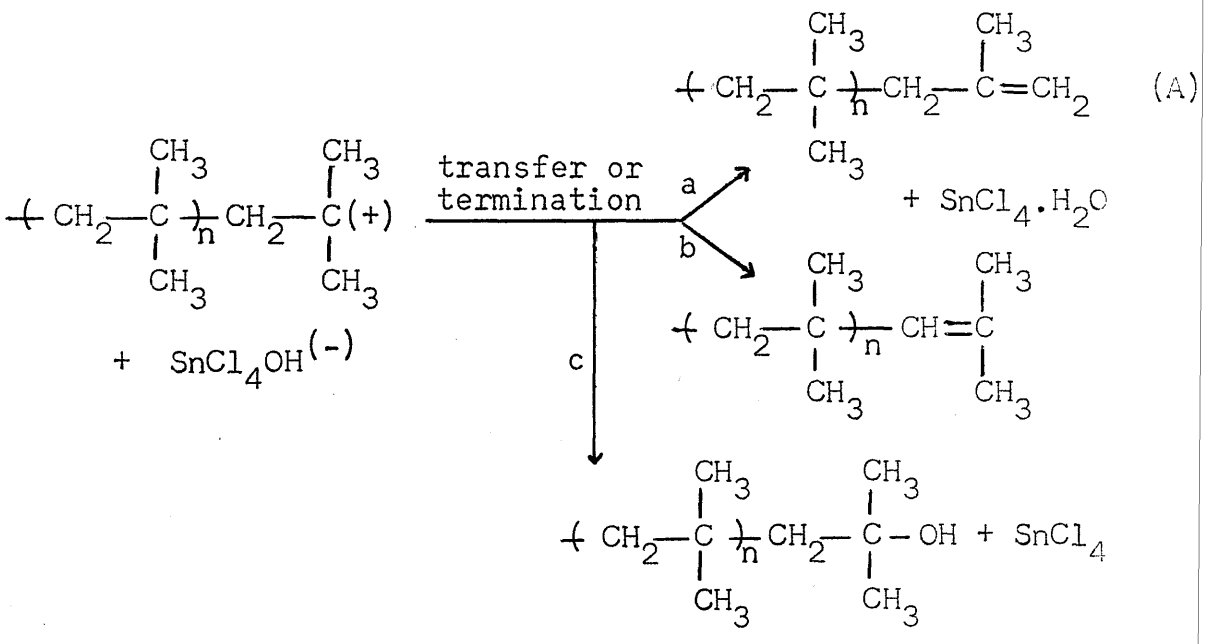
The polymers studied had a molecular weight range, $\overline{M}_n = 3 \times 10^4$ — 4×10^5 ; the double bond

content of these polymers was so small that the double bonds could not be detected in the I.R. spectra, which were all identical.[69] From the structure of the polymer and the mechanism of cationic polymerisation it was predicted that the polymer would exhibit a maximum unsaturation of one double bond per chain. Since the repeat unit in the polymer is,



it is impossible to have internal unsaturation in the absence of anomalous structures. The polymerisation of isobutene by Friedel-Crafts type catalysts, on which a considerable volume of work[34] has been carried out, can be regarded as a "typical" cationic system. Because of the crowding of methyl substituents in the chain structure, isobutene polymerises without the abnormalities of many systems.[34] It has been suggested by Slobodin and Matusevich[70] that some head to head structures may exist in polyisobutene but their presence would depend on the conditions of polymerisation and would not necessarily introduce internal unsaturation. Most evidence suggests that the unsaturation derives from transfer and termination reactions which produce terminal double bonds. Spectroscopic

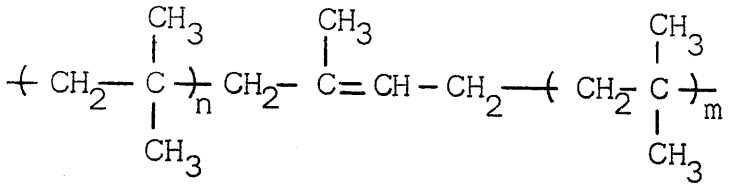
investigations of low M.W. polyisobutene[33,71] have shown the predominance of methylenic unsaturation but it is possible for other termination reactions to occur, e.g. the formation of hydroxyl end-groups.[33,72] The following scheme illustrates the various modes of end-group formation:



From this argument the maximum unsaturation would be one double bond per chain but the concentration of double bonds could be reduced by the participation of reaction (c).

The probable double bond structure (product A above) resembled the unsaturated centre in butyl rubber, the chlorination of which has been previously studied.[29,73]

In this co-polymer of isobutene and isoprene, internal unsaturation is present at each isoprene unit;



It was believed that the chlorination of polyisobutene would be comparable in mechanism to that of butyl rubber.

THE CHLORINATION OF POLYISOBUTENE.

(i) Unfractionated polymers.

The chlorination technique has been fully described in Chapter 2, section 2,(vii). For each polymer a series of chlorinations was carried out in which the only variable was the chlorine concentration. The weight of chlorine in the reacted polymer was measured by counting and the weight per cent of chlorine in the polymer calculated, assuming that the concentration of the polymer solution had remained constant throughout the chlorination and dialysis procedures. The results obtained are summarised in Table 7. Graphs were constructed of Wt.% of chlorine in the product versus Wt.% chlorine in the reaction mixture. These are shown in figures 17 and 18.

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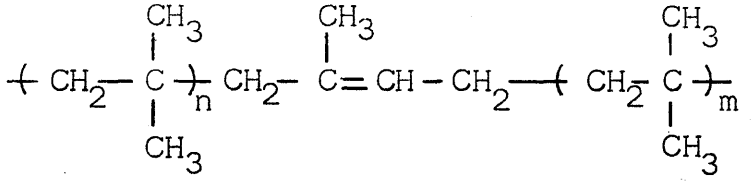

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(ii) Fractionated polymers.

The corresponding data obtained for the fractionated polyisobutenes are given in Table 8 and figure 19.

(iii) Interpretation of results.

The chlorination curves of all the polymers have a similar shape. After an initial steeply-rising part (see figures 17 and 18) the curves level out to give a plateau or a linear portion with a shallow gradient. The rising part of the curve corresponds to samples which have insufficient chlorine present for complete reaction in the time allowed. As the chlorine concentration is increased the situation is reached where further excess of chlorine produces little change in the amount of chlorine incorporated in the product. The height of the plateau is a measure of the extent of chlorination and, providing that only chlorination of the double bond has occurred, the amount of chlorine in the product at this point is a measure of the unsaturation.

In practice the plateau region in the chlorination curves showed a slight gradient and an analogy can be drawn between the radiochlorine curves and the treatment of results by Lee, Kolthoff and Johnson using the iodine chloride method.[9]

TABLE V. REACTION OF UNFRACTIONATED POLYISOBUTENES WITH RADIOCHLORINE.

Wt.% Cl in reaction mixture.	Counts/min. per 10ml. reacted solution	Wt.Polymer.	SA(CCl_4) of Cl supply cpm/mg.Cl	Wt.Cl. mg.	Wt.% Cl in polymer.
1. Polymer IB1					
6.71	239.0	100	2320	0.103	0.103
5.40	126.8	150	814	0.157	0.104
4.45	107.3	150	814	0.132	0.088
3.72	114.0	150	814	0.140	0.093
3.40	85.0	166	570	0.149	0.090
3.00	547.0	236	2360	0.232	0.098
2.50	333.5	158	2360	0.141	0.089
2.18	92.3	150	814	0.113	0.076
1.43	80.3	150	814	0.099	0.066
0.92	158.5	166	2575	0.062	0.037
2. Polymer IB4.					
6.36	103.5	168	814	0.127	0.076
5.15	100.3	168	814	0.123	0.074
4.10	64.8	168	563	0.115	0.068
3.85	60.8	166	563	0.108	0.065
3.62	63.3	168	563	0.111	0.066
2.83	78.9	168	814	0.097	0.058
1.99	80.1	168	814	0.098	0.059
0.65	22.0	168	563	0.039	0.024
0.24	14.7	162	563	0.026	0.016

TABLE 7 CONTINUED.

Wt.% Cl in reaction mixture.	Counts/min. per 10ml. reacted solution	Wt.Polymer. of Cl supply	SA(CCl_4) cpm/mg.Cl	Wt.Cl. mg.	Wt.% Cl in polymer.
3. Polymer IB2.					
5.82	84.1	164	517	0.163	0.099
5.63	80.5	164	517	0.156	0.095
4.29	74.0	164	517	0.143	0.087
3.70	73.6	164	517	0.142	0.086
3.32	71.6	164	517	0.139	0.085
3.00	82.8	164	517	0.160	0.097
2.28	74.5	164	517	0.144	0.087
1.58	59.9	164	517	0.116	0.070
1.12	66.3	164	517	0.128	0.078
0.67	56.5	164	517	0.109	0.066
0.62	54.6	164	517	0.106	0.064
4. Polymer IB3.					
5.50	82.5	166	474	0.174	0.105
3.24	85.5	164	517	0.165	0.100
2.46	76.4	164	517	0.148	0.090
1.46	62.9	164	517	0.121	0.074
0.94	53.9	164	517	0.104	0.063
0.45	42.1	164	517	0.081	0.049

FIGURE 17. CHLORINATION OF POLYMERS IB1 AND IB4.

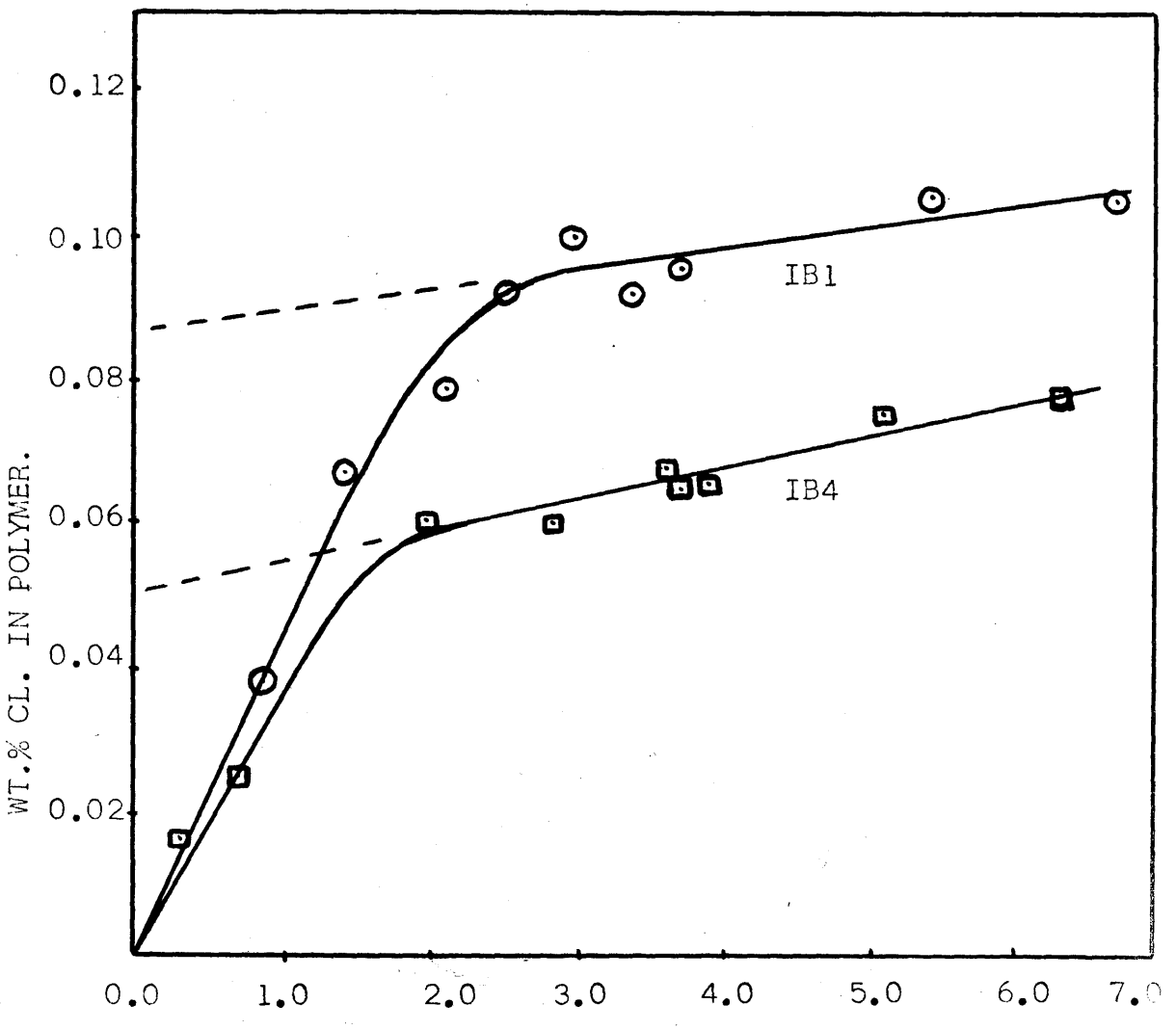


FIGURE 18. CHLORINATION OF POLYMERS IB2 AND IB3.

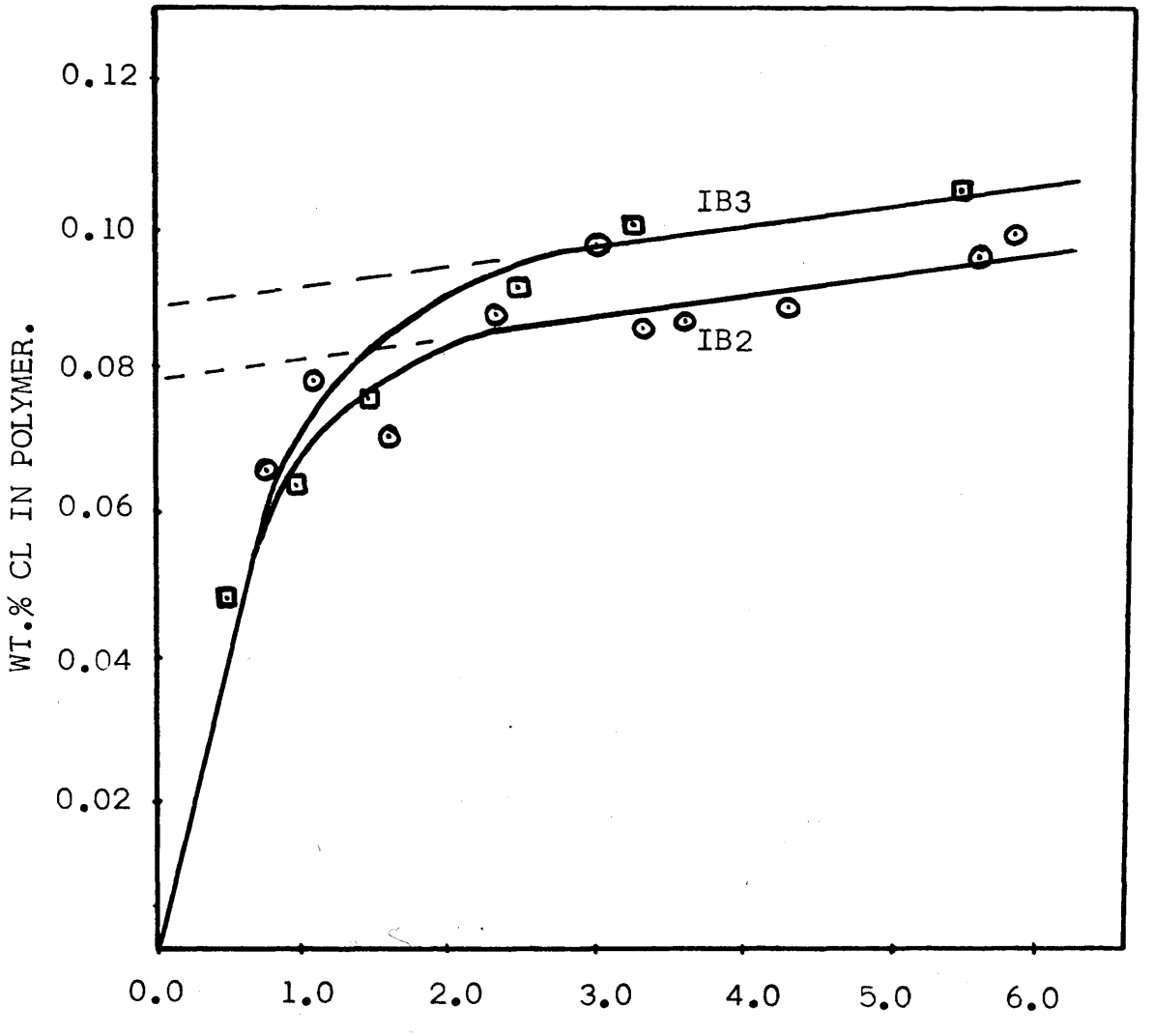


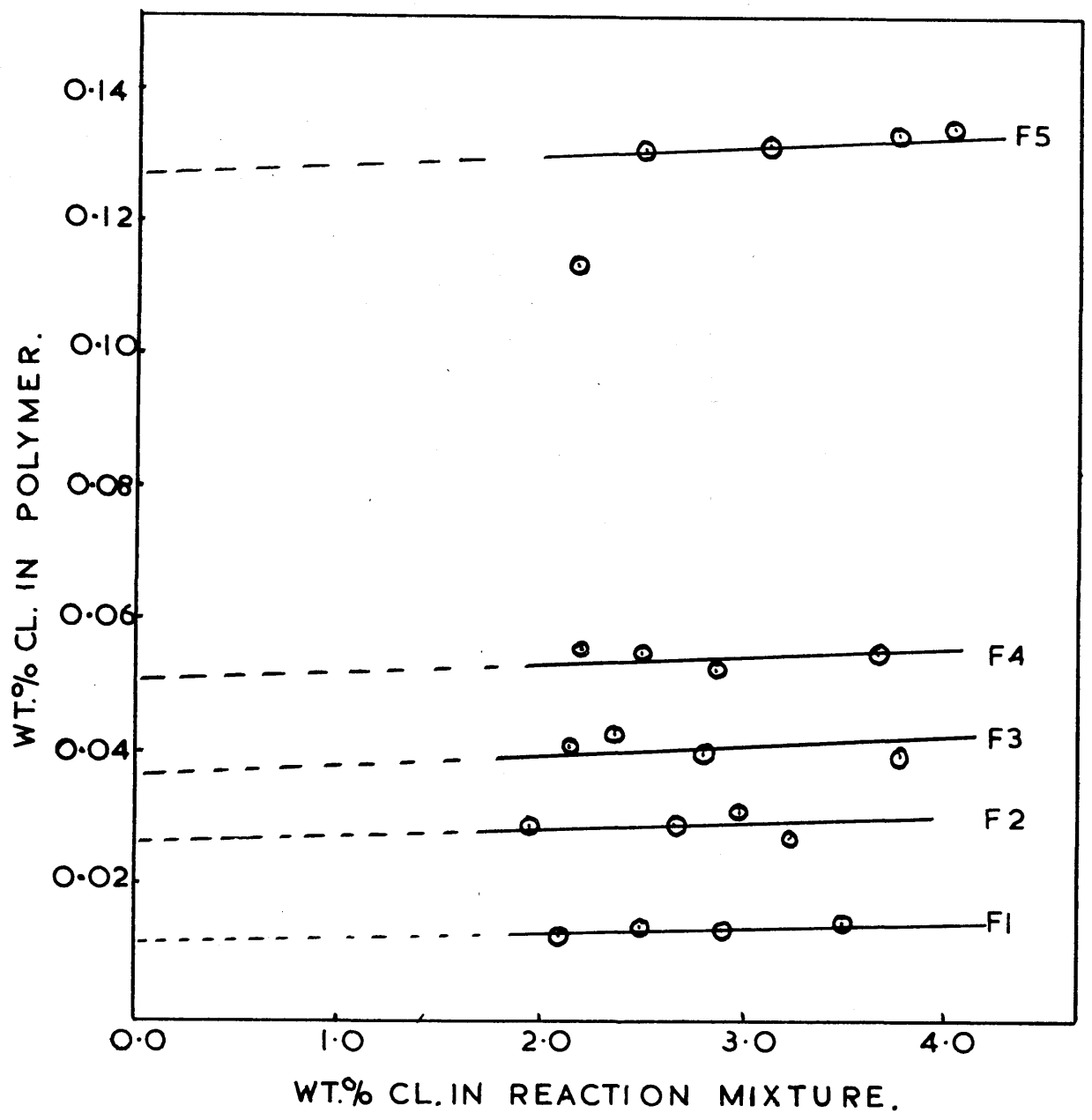
TABLE 8. CHLORINATION OF FRACTIONATED POLYISOBUTENES.

Wt.% Cl in reaction mixture.	Counts/min. per 10ml. solution	Wt.Polymer.mg.	Wt.Cl.mg.	Wt.%Cl in polymer
Polymer F1; SA(CCl_4) = 814 cpm/mg.Cl.				
3.52	18.4	164	0.0226	0.0138
2.90	17.9	168	0.0220	0.0132
2.49	19.1	168	0.0234	0.0139
2.12	17.7	164	0.0219	0.0132
Polymer F2. SA(CCl_4) = 406 cpm/mg.Cl.				
3.25	17.7	165	0.0439	0.0264
2.93	21.4	168	0.0527	0.0312
2.55	20.1	172	0.0495	0.0289
1.99	19.4	168	0.0478	0.0285
Polymer F3. SA(CCl_4) = 406 cpm/mg.Cl.				
3.80	25.5	169	0.0628	0.0372
2.88	26.1	166	0.0643	0.0388
2.36	16.4	95	0.0406	0.0426
2.15	28.1	169	0.0692	0.0410

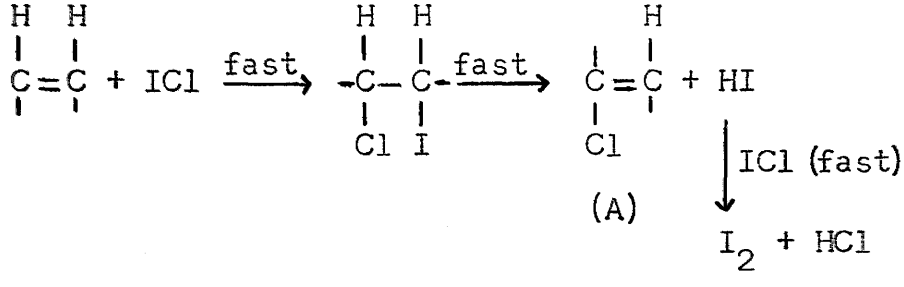
TABLE 8 CONTINUED.

Wt.%Cl in reaction mixture.	Counts/min. per 10ml. reacted solution.	Wt.Polymer mg.	Wt.Cl mg. In polymer.	Wt.% Cl.
Polymer F4 SA(CCl_4) = 406 cpm/mg.Cl.				
3.67	36.2	166	0.0894	0.0538
2.84	34.6	165	0.0854	0.0517
2.47	36.6	166	0.0902	0.0546
2.18	38.1	168	0.0940	0.0560
Polymer F5 SA(CCl_4) = 406 cpm/mg.Cl.				
4.01	90.8	167	0.224	0.134
3.40	90.9	168	0.224	0.133
3.10	88.0	166	0.217	0.131
2.57	90.1	169	0.222	0.131
2.18	76.2	166	0.188	0.113

FIGURE 19. CHLORINATION OF FRACTIONATED POLYMERS.



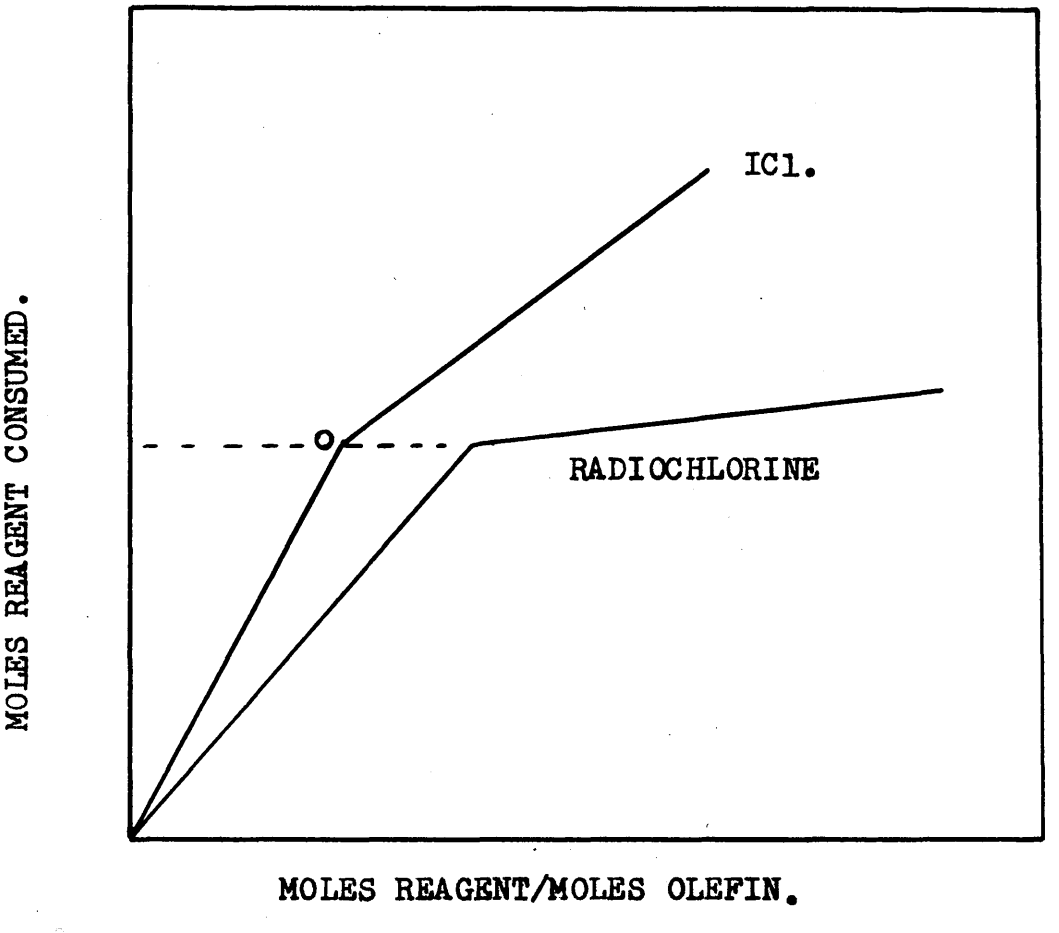
A hypothetical comparison of the radiochlorine and iodine chloride methods is shown in figure 20; a real comparison has been made by McNeill[29] for butyl rubber. It has been shown by Lee, Kolthoff and Johnson that the intercept O of the two linear portions of the graph corresponds to the theoretical unsaturation. The break in the graph is caused by completion of the reaction,



The further increase in consumption of ICl is produced by the slower addition of ICl to product (A).

The chlorination curve is similar in shape but the consumption of chlorine beyond the break in the curve is slower than for the corresponding iodine chloride reaction. McNeill has shown that for butyl rubber the intercept of the two linear parts of the curve again corresponds to a stoichiometric reaction and can be used to derive the molar unsaturation. A similar treatment was employed for the results discussed later in this chapter for model compounds; in the case of the polyisobutenes, the treatment of the chlorination curves was modified slightly.

FIGURE 20. HYPOTHETICAL COMPARISON OF RADIOCHLORINE AND IODINE CHLORIDE RESULTS.



It was more convenient, because of the shallow gradient of the "plateau" region and since it was very difficult to establish the initial portion of the curve due to the very small quantities of chlorine involved, to extrapolate the "plateau" back to the vertical axis, (figures 17 and 18). For these reasons also, in the case of polyisobutene fractions (figure 19), it was considered sufficient to obtain points only in the plateau region. The intercept on the vertical axis was defined as the weight per cent unsaturation, U_W, and the values obtained are listed in table 9.

TABLE 9. WT.% UNSATURATION OF POLYISOBUTENES.

Polyisobutene reference	Molecular Weight. M_n	Wt.% Unsaturation U_W
IB1	45,700	0.085
IB2	49,100	0.078
IB3	40,500	0.089
IB4	100,000	0.049
F1	376,000	0.012
F2	190,000	0.026
F3	125,000	0.036
F4	77,000	0.052
F5	32,000	0.128

(iv) Investigation of side-reactions.

(a) The effect of chlorination on molecular-weight.

The measurement of the molecular weights of reacted polymer samples proved useful since it provided a check on two effects which could interfere with the chlorination results. The first effect is the occurrence of free-radical reactions which would increase the amount of chlorine reacting with the polymer. In such a system some scission of the polymer chains would be expected so that a very sharp drop in the number-average molecular weight would result (see Chapter 5). The second possible effect is diffusion of low molecular weight polymer during the dialysis procedure. The number-average molecular weight is extremely sensitive to low molecular weight material[74] so that an increase in the molecular weight would be observed if diffusion took place. Diffusion would also result in a loss of chlorinated polymer so that the measured unsaturation would be much lower than the true double bond content if results were based on the original molecular weight.

The molecular weights observed for a series of chlorinated polymers are shown in table 10. The samples correspond to different positions on the chlorination curves. The molecular weights are fairly constant for

TABLE 10. EFFECT OF CHLORINATION ON M.W. OF POLYMER.

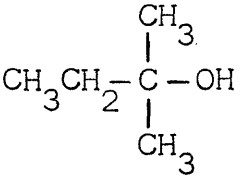
MOLECULAR WEIGHTS MEASURED IN CCl_4 SOLUTION AT 25°C.

Polymer	Wt.% Cl in polymer	Molecular Weight $\bar{M}_n$
IB1.	0	45,700
	0.066	37,000
	0.075	38,000
	0.088	37,000
	0.093	38,000
	0.104	36,000
	0.135	40,000
IB2.	0	49,100
	0.070	39,000
	0.095	35,000
IB4.	0	100,000
	0.056	92,000
	0.058	89,000
	0,059	104,000
	0.073	93,000
	0.076	98,000

each polymer but are in fact slightly lower than the original M.W. values. The difference was attributed to the change in the operating conditions of the osmometer; the original values were measured in toluene at 37°C, but the results in table 10 were obtained at 25°C using carbon tetrachloride solutions since solutions of known concentration in this solvent resulted from the chlorination procedure.

(b) Chlorination of tertiary amyl alcohol.

Tertiary amyl alcolhol has the structure,



and it was investigated in order to determine whether the hydroxyl groups, which were postulated on page 75 as possible end structures, would be susceptible to chlorination under the experimental conditions used. The test on the alcohol would also show whether free-radical substitution of methyl and methylene groups was taking place. The results for the chlorination of t-amyl alcohol are given in table 11.

If all the hydroxyl groups were replaced by chlorine, the amount of reacted chlorine would be 16.14 x 35.5/88mg, i.e. 6.51mg., and the observed count rate of the solution

would be 3,120 cpm. It was concluded therefore that hydroxyl groups are not affected by this chlorination technique and free-radical reactions are negligible.

TABLE 11. CHLORINATION OF TERTIARY AMYL ALCOHOL.

Wt.Alcohol in solution mg.	Wt.Cl added mg.	Counts/min. per 10ml.	SA(CCl_4) cpm/mg.Cl	Wt.Cl reacted. mg.
16.14 (0.02ml.)	7.72	39.1	720	0.081

(c) Scattering of results.

Irreproducible results constituted a very real problem when this study was begun. Most of the scattering was not of a random nature, however, and consisted of some of the polymer samples reacting to much greater extents than others. These high results, which were often more than double the expected ones, were discovered to be related to incomplete evacuation of the reaction tube. It was concluded that extensive side reactions were promoted by traces of air caused by incomplete degassing or slight leakage in the reaction tube. The effect was minimised by employing a more rigorous

degassing procedure.

The further observation was made that if the vacuum was lost completely and air was present at atmospheric pressure the amount of reacted chlorine was approximately equal to that which would have been observed for best vacuum conditions. The amount of chlorine which reacted increased as the vacuum deteriorated, passed through a maximum, and fell back to its original value as the pressure approached atmospheric pressure. This qualitative picture is supported by a more detailed investigation by Haider[31] who observed a similar dependence of the results of chlorination of polystyrene on the degree of evacuation of the reaction tube. This peculiar effect was tentatively explained by the occurrence of free-radical chlorine reactions which were promoted by traces of air but were swamped when oxygen was present in larger quantities.

CHLORINATION OF LOW M.W.POLYISOBUTENE AND MODEL OLEFINS.

The stoichiometry of the chlorination reaction was investigated by studying (a) low M.W. polymers, the unsaturation of which could be determined by other methods and (b) model olefins of known structure.

(a) Low M.W. polyisobutene.

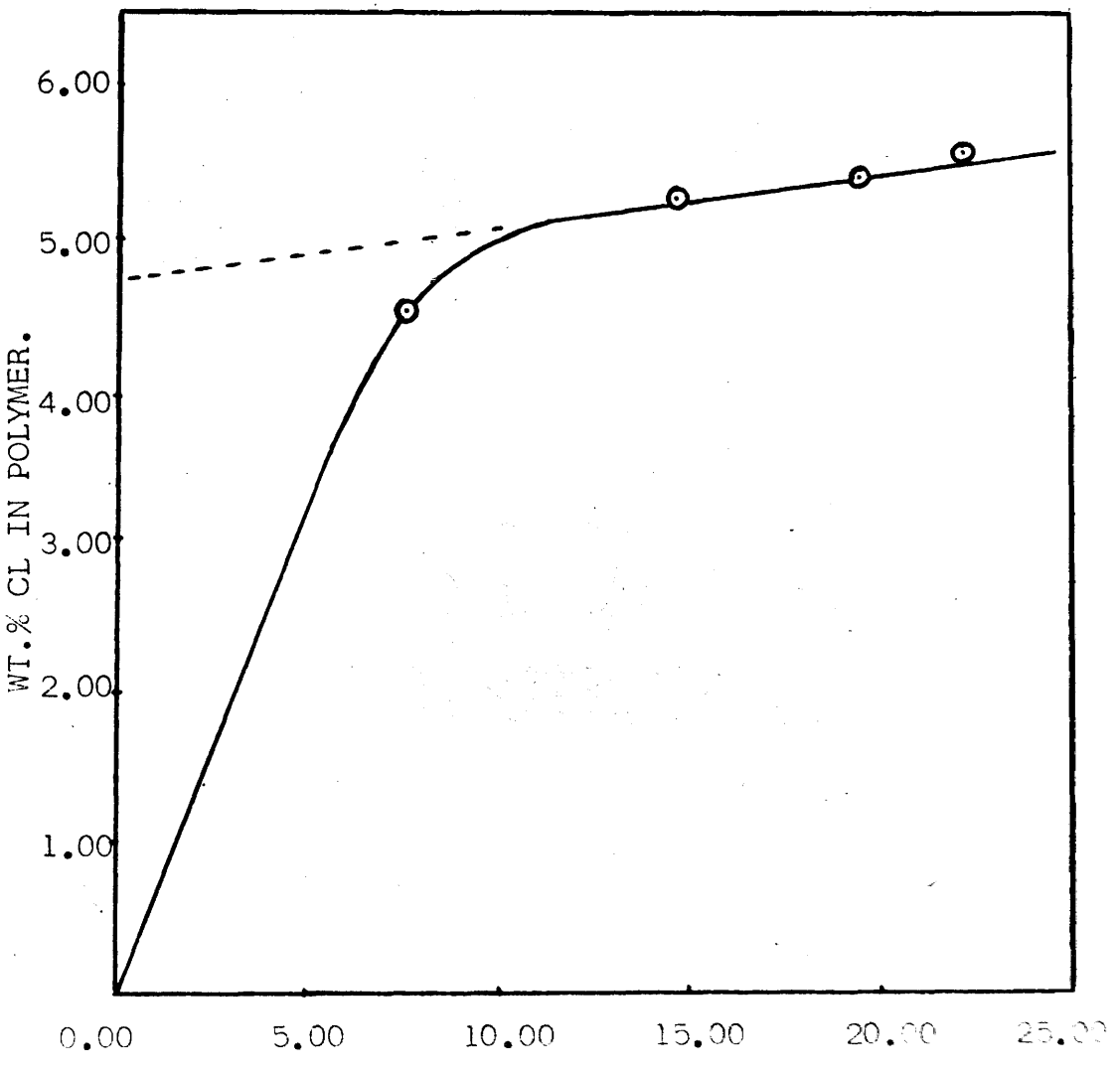
Material of low M.W., $\overline{M}_n < 1{,}000$, was obtained from the degradation of polymer IB4 (Chapter 4). The polymer was chlorinated in the same way as the high M.W. polymers except that, owing to the low M.W., the products were not purified by dialysis. Instead extraction techniques were employed. The results of chlorination are given in table 12 and figure 21. The weight per cent unsaturation, calculated from the intercept on the vertical axis, was 4.75.

TABLE 12. CHLORINATION OF LOW MOLECULAR WEIGHT POLYISOBUTENE.

Wt.% Cl in reaction mixture.	Counts/min. per 10ml.reacted solution.	Wt.Polymer mg.	Wt.Cl mg.	Wt.% Cl in polymer.
$SA(CCl_4)$ = 591 cpm/mg.Cl.				
23.05	753	21.0	1.273	5.71
19.20	711	21.0	1.200	5.42
14.72	691	21.0	1.170	5.29
7.69	588	21.0	0.995	4.55

The molar unsaturation was measured using the iodine-mercuric acetate method of Gallo, Weise and Nelson.[11] This method consists of adding iodine to a polymer solution and measuring the amount of iodine remaining after reaction

FIGURE 21. CHLORINATION OF LOW M.W. POLYISOBUTENE.



by titration against standard sodium thiosulphate solution. The experiment is repeated for a blank solution so that the difference in titres corresponds to the amount of iodine which has reacted with the polymer. The unsaturation is derived from the equation,

$$U = \frac{100(B - S)N.M_1}{3W_p}$$

where U is the mole % unsaturation,

B,S are the blank and sample titres respectively,

M_1 is the monomer molecular weight,

W_p is the weight of polymer (mg.) in the sample,

and the factor 3 accounts for the experimental observation that three atoms of iodine react per double bond in this method.

The results for two determinations are given in table 13.

TABLE 13. UNSATURATION OF LOW M.W. POLYISOBUTENE FROM IODINE / MERCURIC ACETATE TECHNIQUE.

Sample	Wt. Polymer in solution mg.	Titre ml.	Blank ml.	Unsaturation mole %
1	94.5	19.34	22.74	6.72
2	90.5	21.34	24.50	6.50

The relationship between the mole % unsaturation and the weight % unsaturation derived from the radiochlorine technique is given by the equation,

$$U_m = U_w M_1 / 35.5x$$

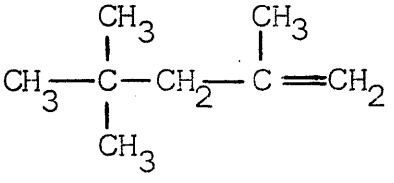
In this equation x is the number of chlorine atoms which are incorporated per double bond. By substituting the mean value of U_m = 6.61, (Table 13) and U_w = 4.75 (page 93) it is found that x = 1.14. The original work on the iodine-mercuric acetate method[11] revealed that the values of unsaturation derived by the technique for double bonds of the isobutene type were approximately 80-100% of the true values. If the value of 6.61 found for low M.W. polymer is 80-100% of the true value, it can be concluded that the value of x is close to unity. This result leads to the important conclusion that the break in the chlorination curve for polyisobutene corresponds to the completion of the reaction between the double bond and one chlorine molecule resulting in the substitution of one chlorine atom into the polymer.

(b) Chlorination of model olefins.

The olefins studied were:

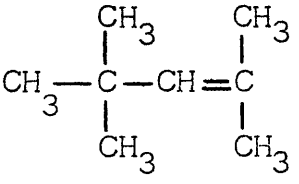
1. Di-isobutene-A, 2,4,4 trimethyl pent-1-ene.

(Koch-Light Laboratories Ltd.)



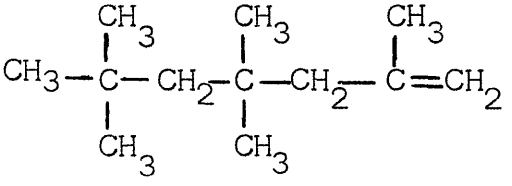
2. Di-isobutene-B, 2,4,4 trimethyl pent-2-ene.

(Koch-Light Laboratories Ltd.)



3. Tri-isobutene, kindly supplied by Dr.J.D.Burnett, I.C.I. (Plastics).

The trimer was probably 2,4,4,6,6 pentamethyl hept-1-ene.



Stock solutions of the olefins were prepared such that 15ml. portions contained approximately 10mg. of olefin. The solutions were chlorinated and purified by repeated thiosulphate and aqueous extraction. It can be easily calculated that for the reaction of one molecule of dimer

with one and two moles of chlorine by substitution, the Wt.% of chlorine in the product would be 24 and 39, respectively. Similarly, the Wt.% Cl values of 17.5 and 30 correspond to the reaction of one and two chlorine molecules with one molecule of trimer.

The observed results are tabulated in tables 14-16 and collected together in figure 22. In contrast to the polymer chlorinations, the curves show a steeply inclined slope beyond the break. Owing to the steepness of the gradients, extrapolation back to the vertical axis was not justified in this case. Two linear portions are clearly defined and the Wt.% unsaturation was calculated by extrapolating these to an intersection. The Wt.% unsaturation values obtained from figure 22 were found to be 28 for Di-isobutene-A, 27 for Di-isobutene-B and 22 for the trimer. These values are about 13% and 25% higher than the theoretical values for incorporation of 1Cl atom per double bond in dimer and trimer, respectively, and clearly fall very far short of the theoretical values for 2 Cl atoms per double bond.

Since the unsaturation of these materials is known, the results can also be illustrated in another way. In table 17 the chlorine content of each reaction product is expressed in terms of atoms of chlorine per double bond.

TABLE 14. CHLORINATION OF DI-ISOBUTENE-A.

Wt. Olefin in reaction mixture mg.	Wt. Cl mg.	Wt.% Cl	Counts/min. 10ml. solution	SA(CCl_4) cpm./mg.Cl	Wt. Cl in product mg.	Wt.%Cl
10.5	2.40	18.6	420	382	1.65	13.6
10.9	5.80	34.7	1120	474	3.54	24.7
10.9	11.20	50.7	1532	474	4.85	30.9
10.6	21.85	67.5	1650	474	5.23	33.2
10.9	31.80	74.4	1651	474	5.23	32.8
10.9	41.40	79.2	1890	474	5.99	35.8
10.9	56.90	84.0	2137	474	6.76	38.6

TABLE 15. CHLORINATION OF DI-ISOBUTENE-B.

Wt. Olefin in reaction mixture	Wt. Cl in reaction mixture	Wt.% Cl	Counts/min. 10ml.solution	SA(CCl_4)	Wt. Cl in product	Wt.% Cl
mg.	mg.			cpm./mg.Cl	mg.	
10.35	3.44	25.0	650	382	2.56	19.8
10.35	6.32	37.9	1244	474	3.94	27.8
10.35	12.55	54.8	1402	474	4.42	30.6
10.35	22.0	68.2	1550	474	4.91	32.5
10.35	41.2	80.0	1770	474	5.60	35.5
10.35	61.7	85.6	1788	474	5.66	35.7

TABLE 16. CHLORINATION OF TRI-ISOBUTENE.

Wt. Olefin in reaction mixture mg.	Wt. Cl in reaction mixture mg.	Wt.% Cl in reaction mixture	Counts/min. 10ml. solution	SA(CCl_4) cpm./mg.Cl	Wt. Cl in product mg.	Wt.% Cl in product
10.2	3.62	26.2	693	474	2.19	17.8
10.2	6.74	39.7	1009	474	3.19	24.0
10.2	11.51	53.2	1170	474	3.70	26.8
10.2	22.85	69.0	1284	474	4.06	28.7
10.2	48.60	82.7	1295	474	4.09	28.9

FIGURE 22. CHLORINATION OF MODEL OLEFINS.

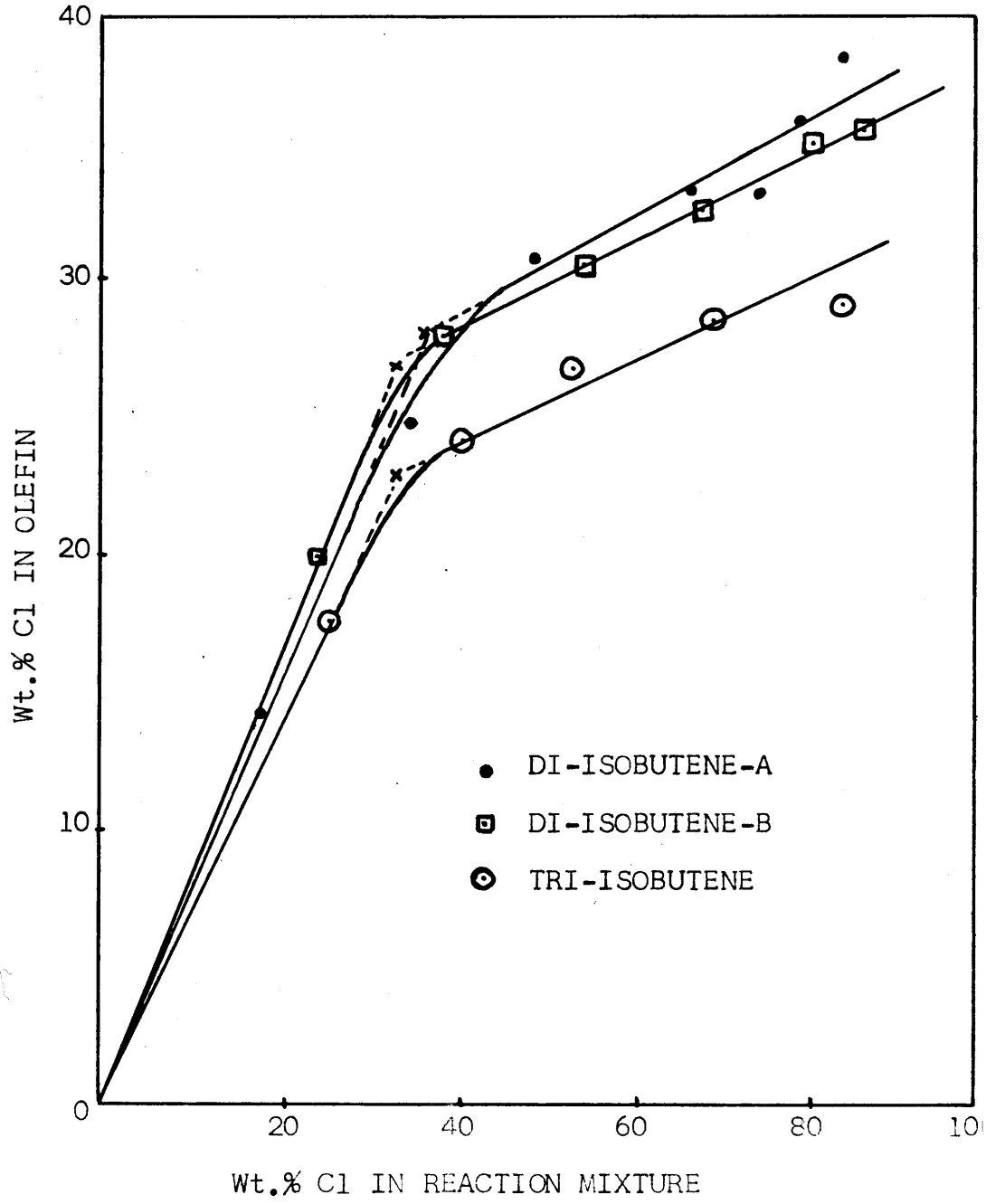


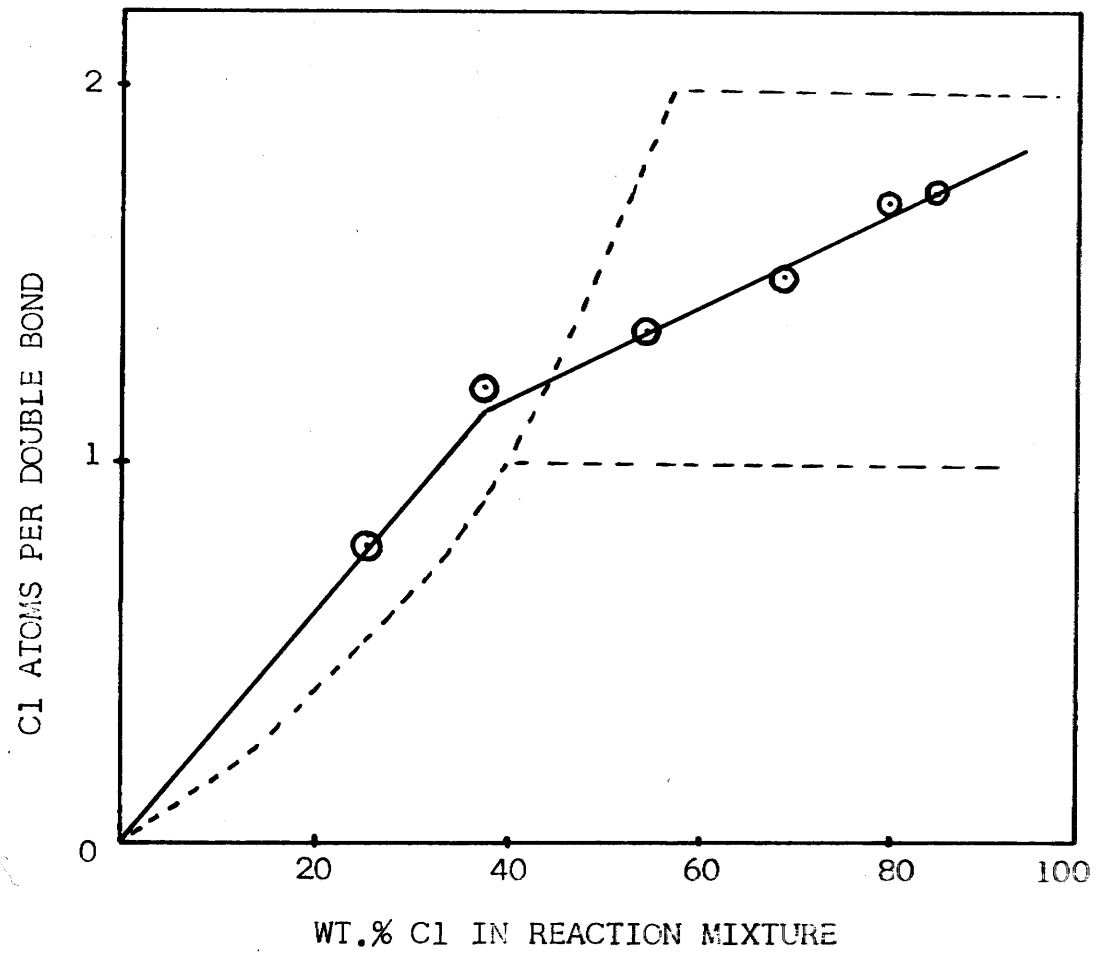
Figure 23 shows the result, for Di-isobutene-B, of plotting this quantity against the chlorine content of the reaction mixture (Wt.%). It is again evident that the intersection is somewhat higher than expected. This figure also shows (dotted lines) the behaviour to be expected for straightforward substitution reactions in which 1 and 2 Cl atoms are incorporated per double bond. The rising part corresponds to mixtures where there is insufficient chlorine to react completely with the double bonds present. A comparison of the theoretical lines in this region with the experimental line shows that, even with the unsaturated compound in excess, more chlorine is present in the product than can be accounted for theoretically in terms of 1 Cl/double bond, but the amount falls very far short of 2 Cl atoms per double bond. Indeed, the theoretical value for 2 Cl/double bond is attained only at extremely high chlorine concentrations.

There appears little doubt, in the light of these considerations, that the true reaction is that of 1 Cl substituting per double bond and that the high results obtained are attributable either to deficiencies in the procedure for decontamination of the product from the relatively large quantities of other radioactive material present, or to side reactions. These results, therefore,

TABLE 17. CHLORINATION DATA FOR MODEL OLEFINS.

Olefin	Wt.% Cl in reaction mixture.	Wt.% Cl in product	Atoms Cl per double bond.
Dimer-A	18.6	13.6	0.49
	34.7	24.7	1.02
	50.7	30.9	1.40
	67.5	33.2	1.56
	74.4	32.8	1.52
	79.2	35.8	1.73
	84.0	38.6	1.95
Dimer-B	25.0	19.8	0.78
	37.9	27.8	1.20
	54.8	30.6	1.35
	68.2	32.5	1.50
	80.0	35.5	1.70
	85.6	35.7	1.72
Trimer	26.2	17.8	1.02
	39.7	24.0	1.48
	53.2	26.8	1.72
	69.0	28.7	1.88
	82.7	28.9	1.90

FIGURE 23. CHLORINATION OF DI-ISOBUTENE-B.



support the conclusion obtained in the experiments with low M.W. polyisobutene, that the break in the chlorination curve corresponds to the introduction of one chlorine atom per double bond rather than two.

DISCUSSION.

The chlorination of olefins.

In order that chlorination data may be applied to the determination of unsaturations, the mechanism and stoichiometry of the reaction must be clearly established. In theory, the polyisobutene can be regarded as a substituted olefin, $R_1CH_3C=CH_2$ or possibly $R_1CH=C(CH_3)_2$. A considerable volume of research has been done on the chlorination of olefins since depending on various parameters the reaction may follow two distinct pathways:

(a) Free-radical addition reaction producing mainly dichloro-products.

(b) Ionic substitution reaction producing monochloro-product.

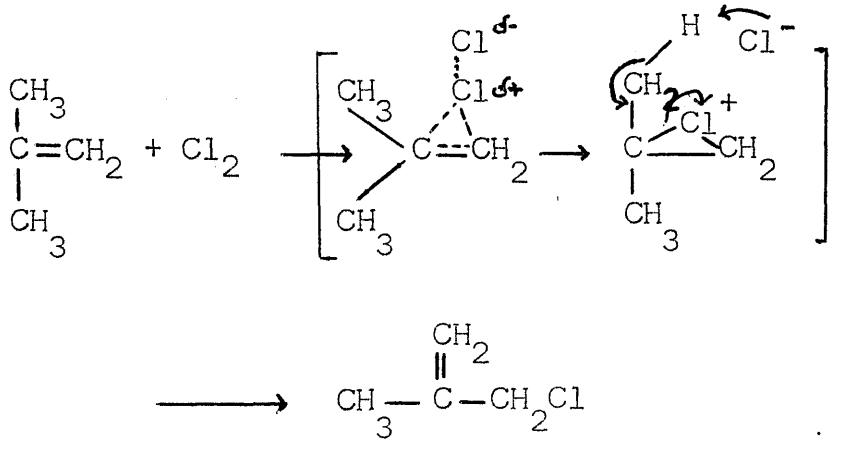
The discovery of the substitution type of chlorination is credited to Sheshukov[75] in 1884 but it is only in recent times that the development of modern analytical and experimental techniques have made possible detailed mechanistic investigations. Isobutene has been the subject

of several investigations[76-79] which show that the main product obtained on chlorination is methallyl chloride (2-methyl 3-chloropropene). Groll et.al.[78,80] compared the chlorination of but-1-ene, but-2-ene and isobutene in a flow reactor using approximately equal w/w chlorine-olefin ratios. The straight-chain butenes gave mainly addition products (55-75%) but isobutene gave 93% substitution product. The substitution reaction proceeded rapidly in the presence of a liquid phase and was not affected by the presence of oxygen. Addition chlorination was induced in the vapour phase by the action of light, and side reactions or further reactions of the primary product were produced if the concentration of chlorine was increased or if the hydrogen chloride by-product was not removed from the reaction mixture.

The duality in mechanism and the effect of various parameters, e.g. olefin structure and concentration, have been recently investigated by Poutsma.[79,81,82] Chlorination was carried out at ambient temperatures using small chlorine-olefin ratios to avoid side reactions. In general the dark chlorination of olefin in the absence of solvent is predominantly radical by nature except for olefins having at least two alkyl groups or one phenyl group substituted at one end of the double bond. The ionic reaction is observed therefore for olefins such as isobutene,

2-methyl but-1-ene, trimethyl ethylene, and tetramethyl ethylene. Dilution of the olefin is a non-polar solvent, e.g. carbon tetrachloride, cyclohexane, favours the ionic pathway. Some olefins which follow the radical mechanism in the absence of solvent change to the ionic mechanism when chlorinated in solution. The chlorination of isoprene[83] is interesting in that both mechanisms take place under certain conditions and a trichloro-product is obtained by substitution at the branched double bond and addition at the unbranched double bond.

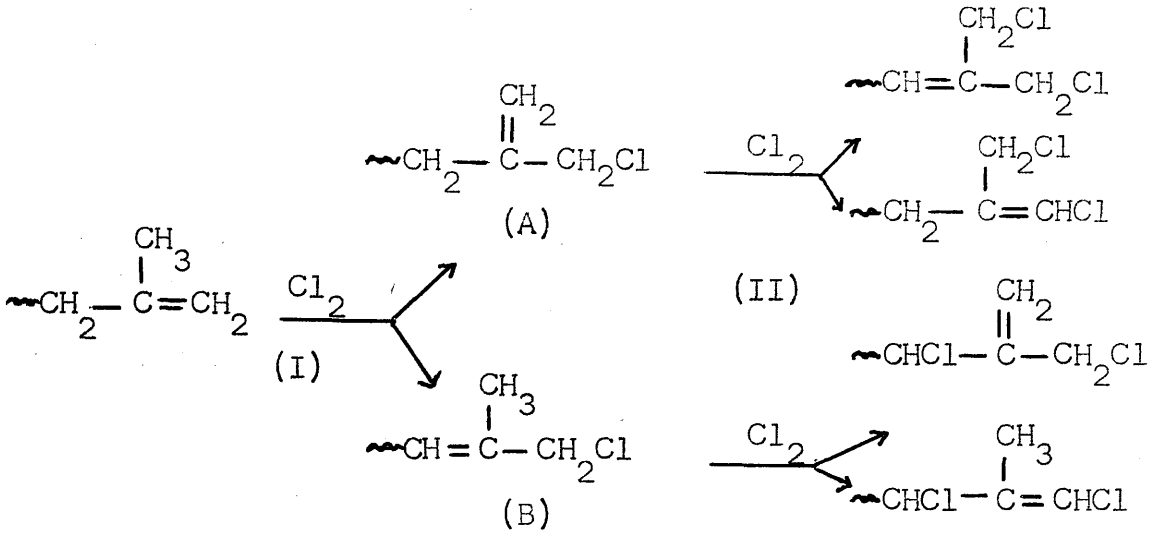
The ionic intermediates of the reaction have been the subject of considerable discussion[82,84-86] but the complex transition state has not been fully elucidated. A plausible mechanism proposed by Ingold[87] involves a cyclic chloronium intermediate instead of the classical carbonium ion:



Although the detailed mechanism is uncertain, the basic reaction between chlorine and polyisobutene is unequivecal. The ionic pathway was ensured by the choice of experimental conditions; carbon tetrachloride provided the non-polar medium which favours the ionic mechanism and oxygen was eliminated since, although it has not been found to interfere with the substitution, its presence could induce unwanted side reactions. As a further safeguard against radical reactions, the chlorinations were carried out in the absence of light.

The extent of chlorination.

The chlorinations in the present study differed from those discussed above in that the chlorine was present in greater concentrations and it has been suggested[78] that further reaction may take place. The possibility of side-reactions of the polymer with either the excess chlorine or hydrogen chloride produced by the primary reaction, and further reaction of the double bond must be considered. McNeill[29] has concluded that, in the similar chlorination of butyl rubber, the double bond reacts stepwise with two chlorine molecules to produce a dichloro-product. For polyisobutene therefore the following reaction scheme might prevail.

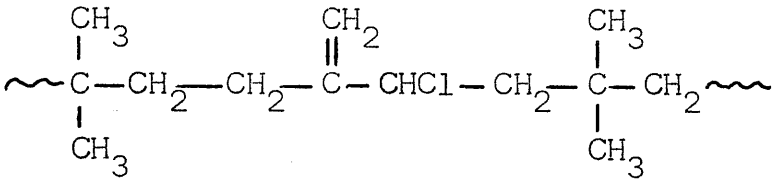


The dichloro-products could react further by a similar mechanism. It is evident that the reactivity of the double bond in the primary allyl product and steric factors are going to control the rate of further reaction. Poutsma[82] found that the addition of chlorine to allyl chloride proceeded 450 times slower than the reaction with but-1-ene.

The relationship between the shape of the polyisobutene chlorination curves and the reaction scheme outlined above has been investigated by studying model olefins and low M.W. polymer. The break in the chlorination curve clearly corresponds to the completion of the primary reaction, I. Secondary reactions, II, taking place at a very much reduced rate may be responsible for the shallow gradient of the "plateau" region of the curve, but this could also be caused by inadequacies of the purification technique as

the amount of chlorine is increased.

The reason for the difference in the stoichiometry between the butyl rubber chlorination[29] and the present study is obscure. A speculative explanation is that the difference depends on subtle steric factors; if the major product of polyisobutene chlorination was structure (B) above, the double bond would be more shielded than the corresponding product in butyl rubber chlorination,



Molar unsaturation of high M.W. polyisobutene.

The mole % unsaturations were calculated from the equation,

$$U_M = 56U_W / 35.5x \quad \text{double bonds per 100 chain units,}$$

in which the value of x was now accepted as unity. The unsaturation was also calculated in terms of double bonds per chain from the equation:

$$N = U_W \bar{M}_n / 3.55 \times 10^3 \quad \text{double bonds per chain.}$$

The observed values of U_M and N are shown in table 18. The data show that the unsaturations correspond to 1.0 - 1.4 double bonds per chain. The deviation from unity

increases with the molecular weight of the polyisobutene. If unity is accepted as the true unsaturation, most polymers show an error of at least 10% which could be explained by addition reactions competing with the ionic substitution, cf. in isobutene, approximately 90% reacts by substitution and 10% by the addition mechanism. The enhanced error with increase in M.W. reflects imperfections in the purification technique or possibly the increasing importance of side reactions.

TABLE 18. MOLAR UNSATURATION OF POLYISOBUTENES.

Polymer	Molecular Weight $\overline{M}_n$	$\frac{10^5}{M_n}$	Mole % Unsaturation	Double bonds per chain
IB1	45,700	2.19	0.134	1.09
IB2	49,100	2.04	0.123	1.08
IB3	40,500	2.47	0.140	1.01
IB4	100,000	1.00	0.080	1.43
F1	376,000	0.266	0.018	1.21
F2	190,000	0.526	0.040	1.36
F3	125,000	0.800	0.056	1.25
F4	77,000	1.299	0.082	1.13
F5	32,000	3.120	0.202	1.15

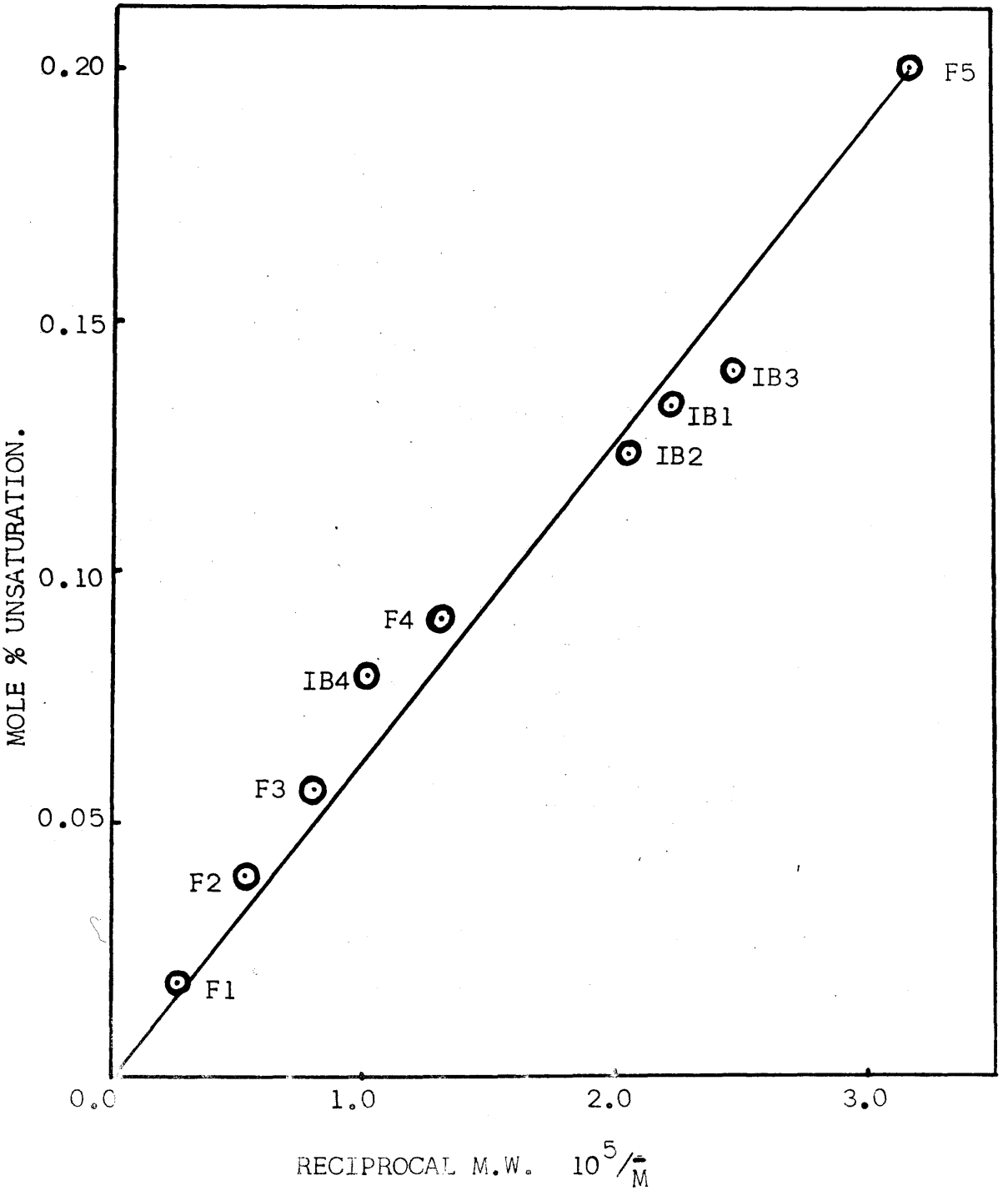
Location of double bonds.

The nature of the unsaturation can be established readily from the experimental results by relating the molar unsaturation to the molecular weight. Figure 24 shows a graph of mole % unsaturation versus reciprocal molecular weight. The straight line relationship passing through the origin proves that the unsaturation is exclusively terminal. For random unsaturation in the chain, the unsaturation would have been independent of the number of chain ends so that a straight line parallel to the horizontal axis would have been observed.

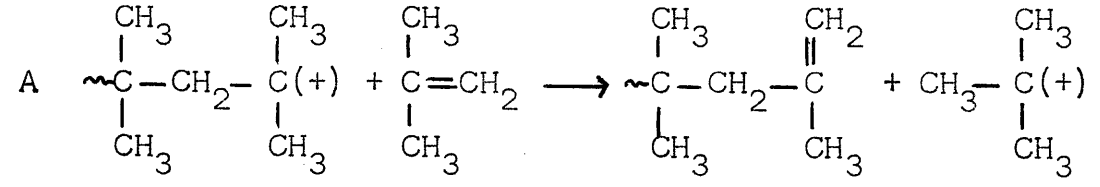
Termination Mechanism of cationic polymerisation.

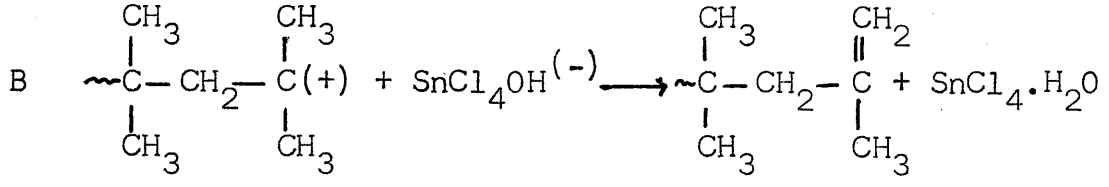
The quantitative information concerning the degree and nature of the unsaturation can be correlated with the known chain breaking reactions in cationic polymerisation. Reilly and Pepper[15] have distinguished between spontaneous proton transfer and monomer transfer by measuring the unsaturation in oligomeric polystyrene. The unsaturation in polyisobutenes was found to be one double bond per chain which clearly shows that the main chain-breaking reaction is proton transfer. Termination reactions between the propagating cationic species and the hydroxyl groups in the anionic catalyst residue do not occur therefore under the polymerisation conditions used. Transfer reactions leading

FIGURE 24. DEPENDENCE OF MOLAR UNSATURATION OF POLYISOBUTENE ON MOLECULAR WEIGHT.



to the formation of saturated end groups derived from solvent[88] are also unimportant in this system. The terminal unsaturation could be obtained from either transfer reaction A, or termination reaction B involving collision of the cationic and anionic fragments, or both.





Further resolution of the transfer and termination reactions can be made by reference to the kinetic investigations of the polymerisation of isobutene using $SnCl_4$ as catalyst.[1,89] Thus Norrish and Russell found that the rate of monomer transfer was small and that the main chain breaking reaction was the termination reaction B. The suggestion [90] that the kinetic data could be explained by chain breaking reactions involving the catalyst hydrate rather than the anionic fragment was disproved by Plesch[34] in favour of the original conclusion by Norrish and Russell. The present study does not distinguish the two mechanisms of double bond formation, but it does give quantitative

proof to the conclusion of Norrish and Russell that every chain-breaking reaction results in the formation of a terminal double bond.

CHAPTER 4.

THERMAL DEGRADATION OF POLYISOBUTENE.

INTRODUCTION.

The relationship between the structure of polymers and their degradation behaviour has been discussed in Chapter 1. For polymers which degrade by depolymerisation two extremes of behaviour have been found. In the first case the primary radical formed on initiation unzips completely to give quantitative conversion of the polymer into monomer. The second type of reaction involves random chain scissions and transfer controlled depolymerisation which result in the formation of a wide spectrum of products and consequently very low monomer yields. The two schemes are easily distinguished by studying the products of degradation, the molecular weight changes on degradation and the kinetics of the process.

The degradation of polyisobutene and other polyolefins has been reviewed by Madorsky;[38] the mechanism of breakdown can be explained qualitatively in terms of the polymer structure. For unzipping to monomer to occur as in polymethyl methacrylate the polymer radical must be stabilised by

chain substituents and have hydrogen atoms which are relatively unreactive with respect to transfer. When the radical is not stabilised, as in the case of polyethylene and polypropylene, the availability of reactive hydrogen atoms leads to transfer reactions with which the unzipping process cannot effectively compete. Polyisobutene is intermediate between the two extremes. The pair of methyl substituents gives some stability to the radical and hinders transfer reactions by shielding the hydrogen atoms. Because of the quaternary carbon atom in the chain, polyisobutene degrades at lower temperatures than polypropylene and polyethylene.

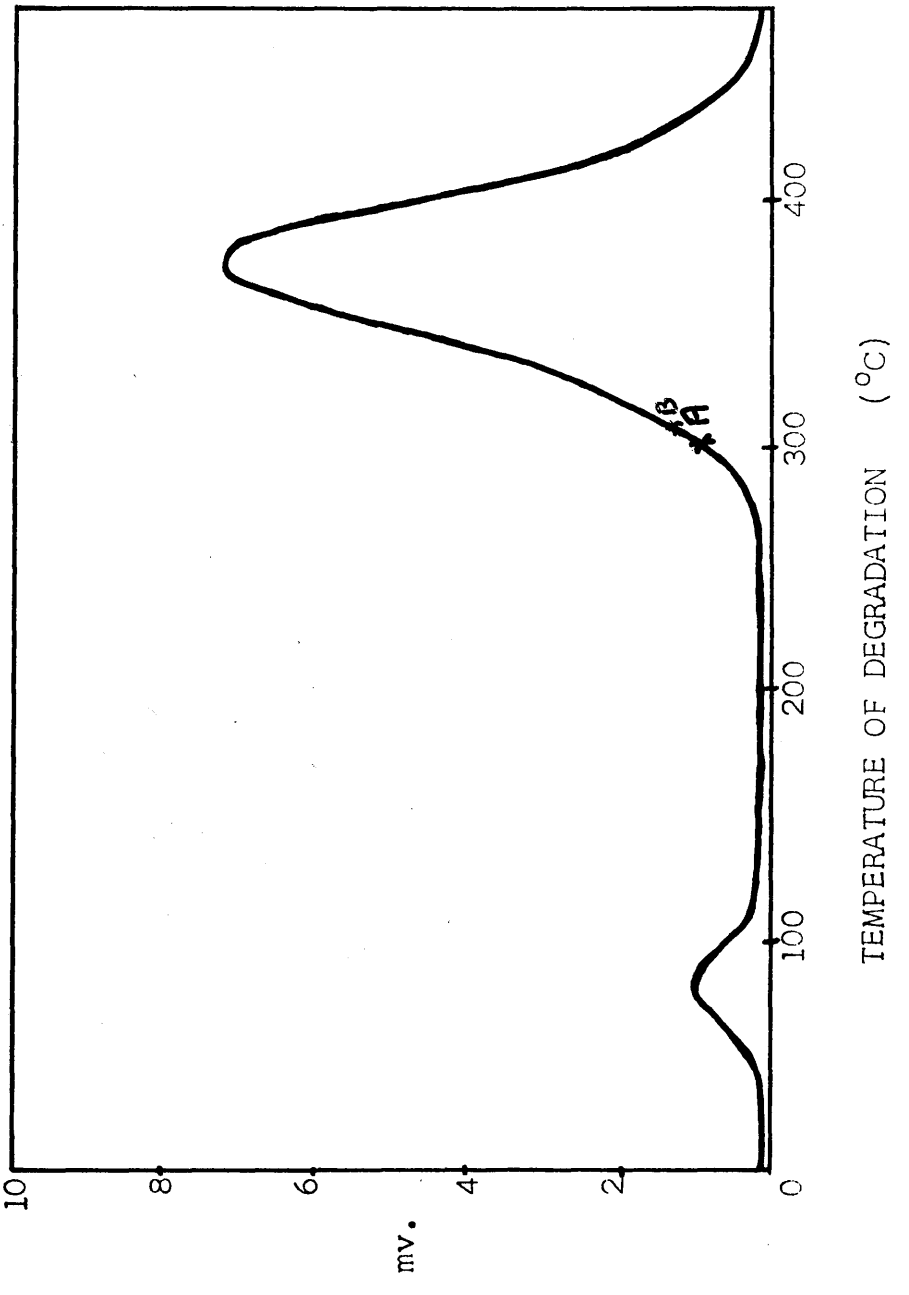
In this chapter, a survey of the degradation behaviour of polyisobutene is made as a prelude to the study of chlorinated derivatives. Emphasis is placed on rate characteristics and comparison is made between the pressure method used in this study and the weight-loss technique used by Madorsky[54] and other workers.[55]

TEMPERATURE-PROGRAMMED DEGRADATIONS.

The use of this technique has been described in Chapter 2, section 3 (iv). Traces of pirani voltage versus temperature were obtained for a series of heterodisperse and fractionated polymers. The charts were almost identical for every polymer and the shape is illustrated in figure 25. A small peak was usually observed at low temperatures corresponding to the evolution of volatile impurities. The whole degradation process was represented by a single large peak which began at 270^{o}C. There was no residue left in the degradation tube but part of the degraded polymer appeared as a non-volatile fraction in the cooled upper half of the tube.

An approximate value of the activation energy was derived from the initial part of the main peak. The pirani voltages at points A,B, (Fig. 25), from which the value of the base-line was subtracted, were converted into pirani pressures and hence into true pressures using the calibration chart shown in figure 14. The true pressures were used as values of the initial rates for the temperatures, which were found from figure 12, corresponding to points A,B. It was assumed that the change in weight of the sample between A and B was negligible. The

FIGURE 25. TEMPERATURE PROGRAMMED DEGRADATION OF POLYISOBUTENE.



activation energy was calculated from the equation (2) below which is easily derived from the Arrhenius equation (1). The data obtained are presented in table 19.

$$k = Ae^{-E_A/RT} \quad ....(1)$$

$$E_A = -4.574 \times 10^{-3} \frac{(\log P_A - \log P_B)}{(1/T_A - 1/T_B)} \quad k.cal.mole^{-1} ...(2)$$

where E_A is the activation energy,

P_A, P_B the pressures at points A and B

and T_A, T_B the temperatures at points A and B respectively.

The values of activation energy obtained by this treatment, i.e. 51-54 $k.cal.mole^{-1}$ were in good agreement with that obtained in the following section and that found by Madorsky.[38]

DEGRADATION BY WEIGHT-LOSS METHOD.

The amount of polymer volatilised for different times of degradation in the temperature range 300 - 320°C was determined by weighing the degradation tube before and after degradation. The cold-ring fraction was removed from the top part of the tube and the tube re-weighed. It was

TABLE 19 - ACTIVATION ENERGY FROM TEMPERATURE PROGRAMMED DATA.

Sample	Temperature ^{o}A	$\frac{10^3}{T}$	Pirani voltage mv.	Pirani pressure torr	True pressure torr	Log.(P)	Activation energy k.cal.mole^{-1}
IB4	598.7	1.670	2.00	0.0120	0.0041	-2.3872	53.8
	611.2	1.636	4.40	0.0282	0.0103	-1.9872	
F4	579.9	1.724	1.05	0.0063	0.00205	-2.6882	51.4
	592.4	1.688	2.45	0.0148	0.0052	-2.2840	

convenient to classify those products which were gaseous in vacuo at room temperature as volatiles and those which were volatile at the temperature of degradation but non-volatile at room temperature as cold-ring fraction. It was possible therefore to obtain the distribution by weight of volatiles, cold-ring fraction and residue for various time intervals. The results obtained for polymer IB4 are summarised in table 20. The % degradation was defined as the % weight loss of the sample which is equal to,

$$100\ (W_{Volatiles} + W_{Cold\text{-}Ring})\ /\ W_{sample}.$$

The final column in table 20 shows the distribution of products into volatile and cold-ring fractions. The scattering of these distributions reflects the inaccuracy of weighing small amounts of polymer sample in a large degradation tube. Figure 26 illustrates the weight-loss treatment. A qualitative representation of the rate characteristics is given in figure 27 which shows the pirani pressure as a function of the extent of degradation for several temperatures.

The energy of activation was deduced from the data shown in figure 26. Since a linear relationship existed between log.(% residue) and time, first order kinetics were

TABLE 20 - DEGRADATION OF POLYISOBUTENE IB4 BY WEIGHT-LOSS.

Temperature of degradation °C	Weight sample mg.	Duration of degradation min.	% Degradation	%Volatiles in products
300	97.4	120	15.4	35.0
300	96.2	200	23.0	32.2
300	98.6	240	26.0	43.9
300	102.6	300	41.9	42.7
305	97.8	60	17.8	32.0
305	103.2	100	20.0	27.6
305	104.8	120	24.9	40.2
305	98.6	180	28.7	39.0
305	95.7	240	39.1	43.8
310	98.8	60	18.5	45.9
310	97.5	120	32.2	42.5
310	96.8	240	51.3	47.1
310	102.3	300	62.7	41.8
319	101.6	60	27.0	50.0
319	95.8	120	49.0	33.5
319	96.3	240	79.1	30.2
319	100.2	300	85.6	39.0

FIGURE 26. DEGRADATION OF POLYMER IB4 BY WEIGHT-LOSS TREATMENT.

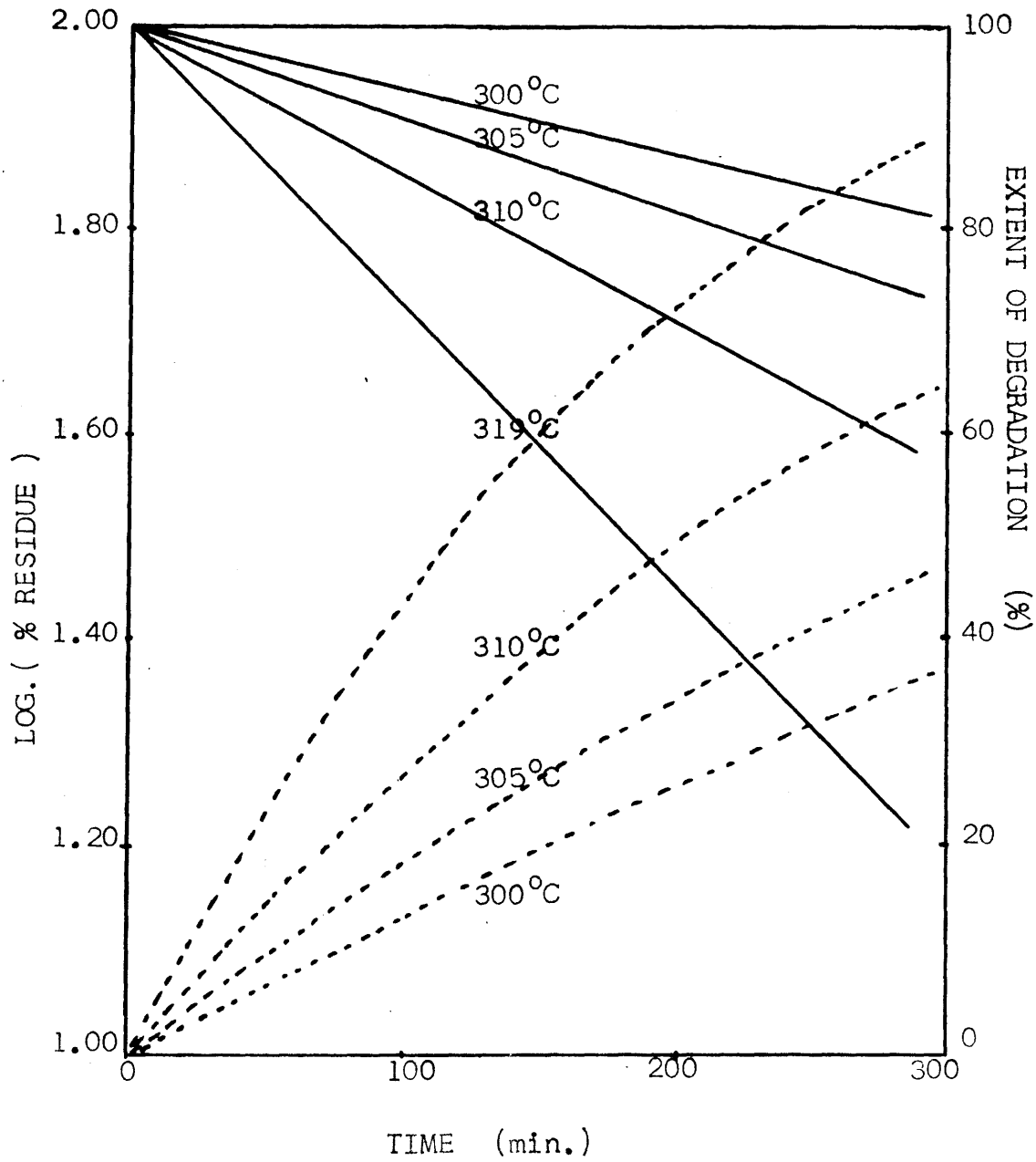
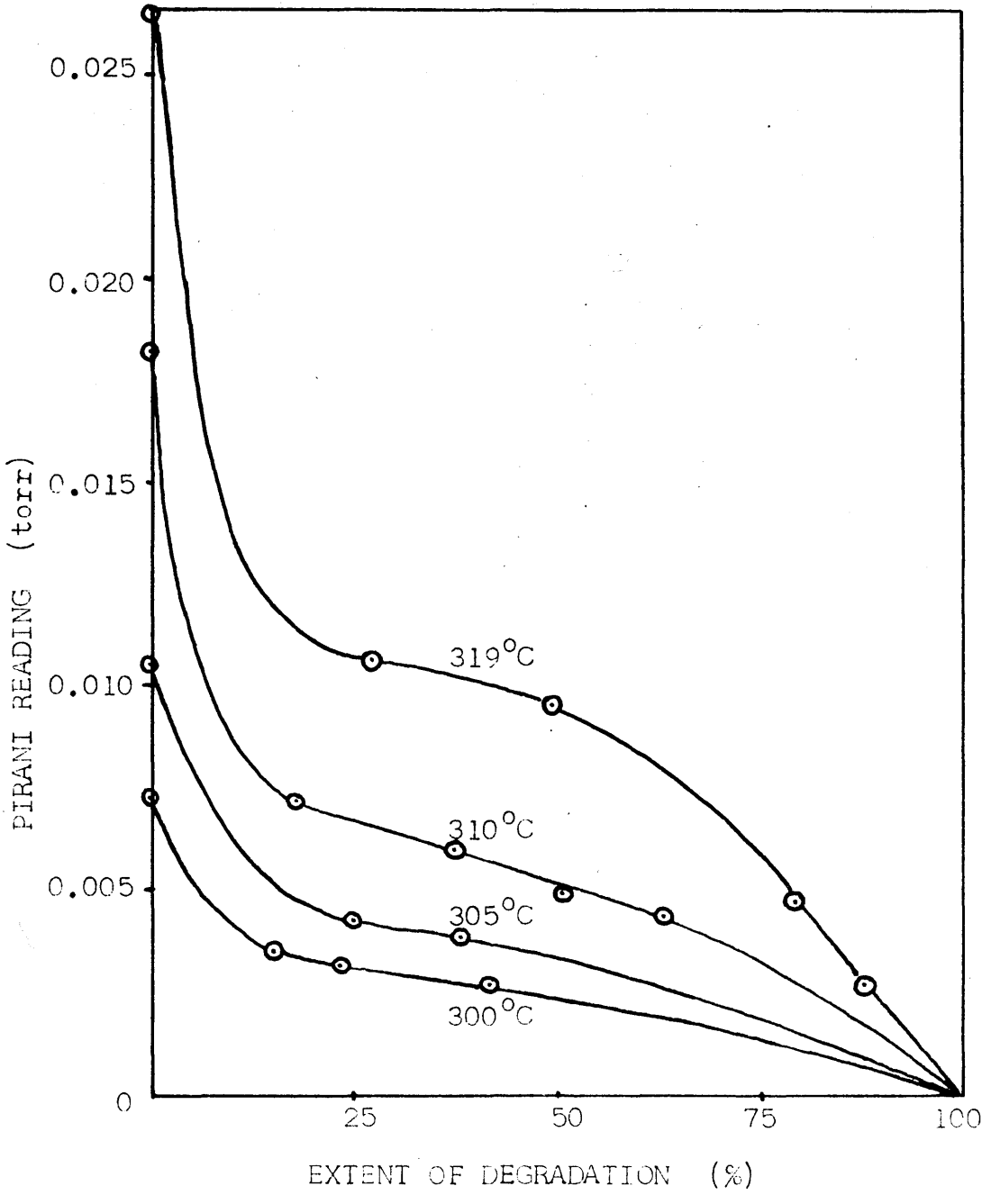


FIGURE 27. RATE CURVES FROM PIRANI MEASUREMENTS FOR POLYMER IB4.



applicable and the slopes of the graphs were a measure of the rate constants. Hence,

E_A = -4.574 . 10^{-3} x slope (log.k vs $^1/T$ plot) k.cal.mole^{-1}

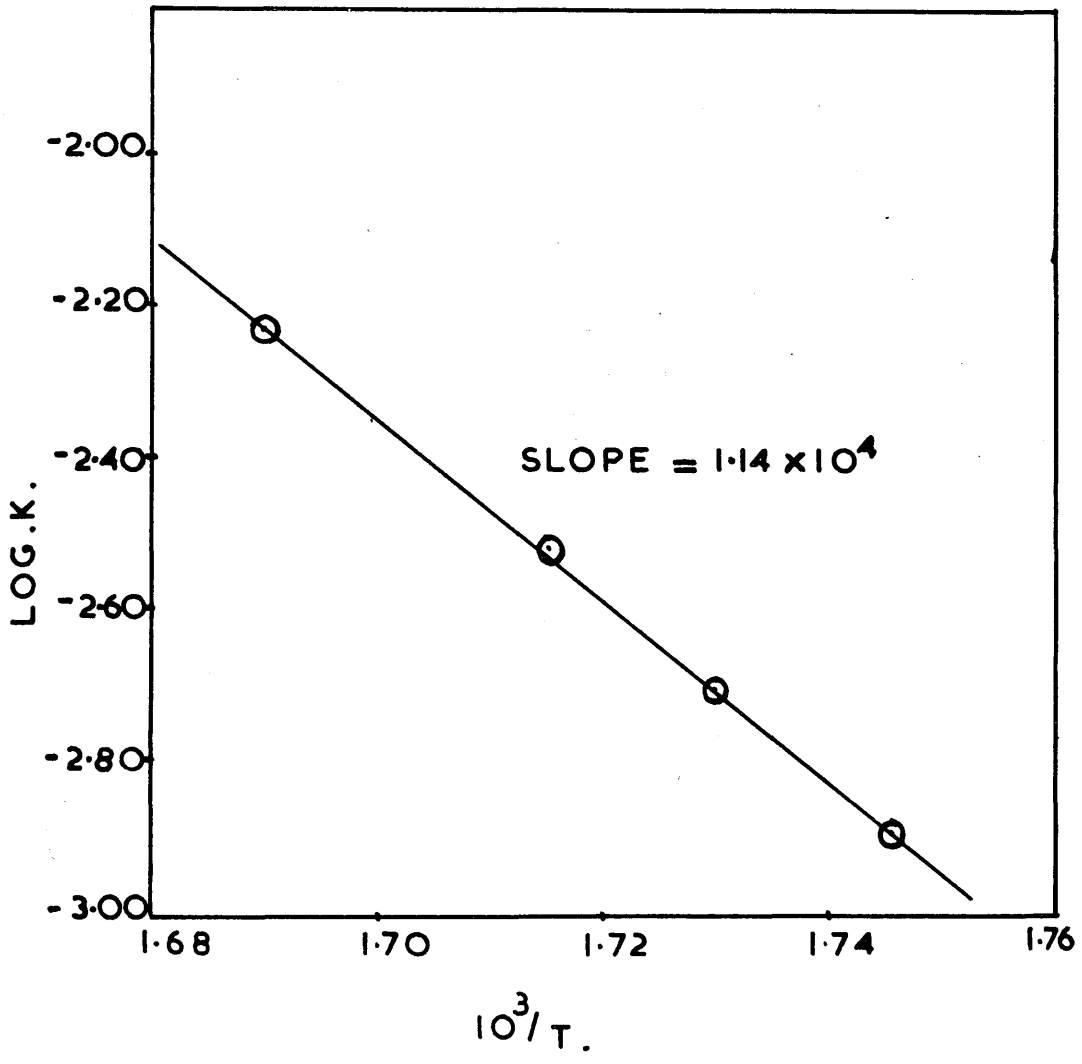
(cf. equation (2) above).

This treatment is presented in table 21 and figure 28. The value of the activation energy was 52 $\pm$ 5 k.cal.mole^{-1}.

TABLE 21. KINETIC DATA FROM FIGURE 26.

Slope from Fig.26 x 10^4	Rate Constant x 10^3	Log K	Temperature ^oA	Reciprocal Temperature $10^3/T$
-5.9	1.36	-2.8668	573	1.745
-8.3	1.91	-2.7186	578	1.730
-13.5	3.11	-2.5072	583	1.715
-25.5	5.86	-2.2321	592	1.689

FIGURE 28. ARRHENIUS TYPE PLOT OF POLYISOBUTENE DEGRADATION DATA.



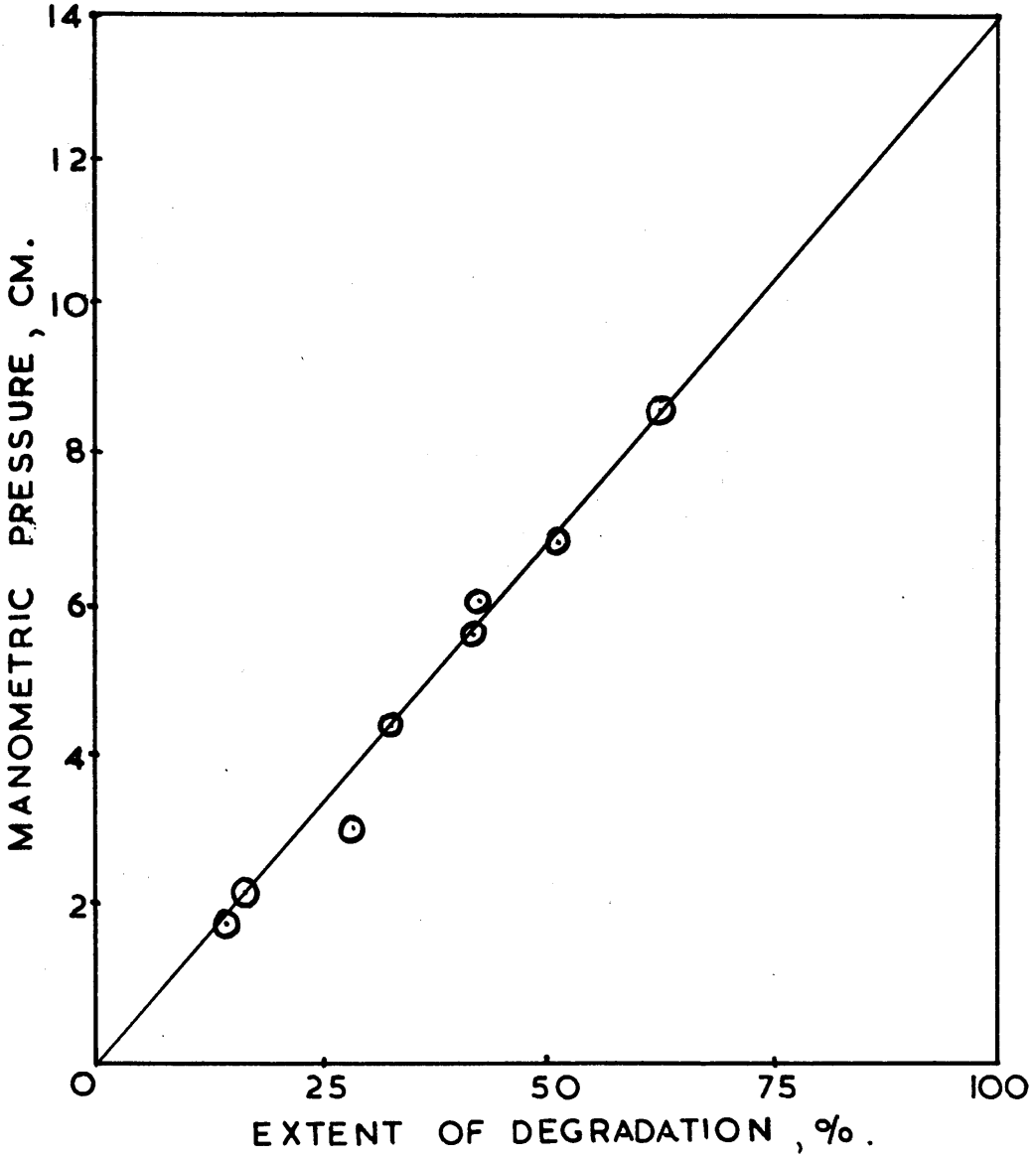
DEGRADATION BY PRESSURE METHOD.

The study of reaction rates by the weight-loss method was found to be tedious and irreproducible; by the introduction of a pressure gauge (see page 65) into the apparatus it was possible to obtain complete % degradation-time curves in a single experiment. The use of the pressure gauge was justified by the observed linear relationship between the manometric pressure of volatiles and the extent of degradation measured by weight-loss. This is illustrated in figure 29. On prolonged heating polyisobutene degrades completely to volatile and cold-ring products. The extents of volatilisation at intermediate times, t, were determined by expressing the pressure, P_t, as a percentage of the pressure observed for complete degradation, P_∞. It followed from the evidence presented in figure 29 that the extents of volatilisation (%) and degradation (%) were equivalent in the case of polyisobutene: i.e. the ratio of volatile to cold-ring production remained constant throughout the degradation. The pressure gauge was calibrated (pages 66 - 67) so that the pressure could be converted into the weight of volatile products. It was determined that,

1cm.pressure at $24^{\circ}C$ = 2.61 mg.volatiles;

cf. 1cm.pressure at $24^{\circ}C$ = 1.66 mg.isobutene;

FIGURE 29. RELATIONSHIP BETWEEN TOTAL PRESSURE OF VOLATILES AND EXTENT OF DEGRADATION.



so that there were present in the volatiles species of higher molecular weight than isobutene. It was assumed that this relationship that equal manometric pressures of degradation volatiles and isobutene had a mean ratio of 1.57 would be approximately valid for pirani pressures, so that in the calibration curve in figure 15 the rates of isobutene transfer corresponding to various pirani readings were converted into rates of volatile production by multiplying by the factor, 1.57. It was possible therefore to obtain rates of degradation in the unit, mg. volatiles/min., from the observed pirani readings during degradation. In order to equate the degradations of slightly different weights of polymers the rates were usually expressed in the unit, % original weight degraded per minute, i.e. %/min., by dividing the rate in mg./min., by the weight of volatiles (mg.) obtained on complete degradation and multiplying by 100. Rates of degradation were alternatively estimated from the % degradation-time data by calculating the average rates for successive time intervals. It was found, in fact, that the two methods of rate determination gave the same results at low rates of degradation, but at high initial rates the rates derived from pirani readings were considerably higher than those obtained from the % degradation-time results. This is discussed further on page 132.

The results obtained for a series of polymers are given in tables 22 - 24; the rates were calculated from the pirani pressures. The similarity in rates of degradation is shown in figures 30 - 32. The degradation behaviours of the polymers were almost identical and most differences were related to changes in the experimental conditions; the figures 30 - 32 group together degradations carried out in three different degradation tubes and the unavoidable use of different tubes caused small differences in the rates by affecting the internal temperature of the tube relative to the external thermocouple. The only distinct change in behaviour was exhibited by the lowest molecular weight polymer, F5, the end-groups of which had been chlorinated as described in Chapter 3. An initially faster rate was observed for this sample.

The results for polymer F1 were recalculated using the % degradation-time data and are summarised in table 25. The differences in the results obtained for this polymer are shown in figure 33. The rate obtained from the pirani pressures (table 23) are obviously higher than the true rates in the early stages of degradation; since the extent of degradation after 15 minutes was 8.7%, the mean rate during this interval, which must exceed the rate at the end of 15 minutes, was 0.58%/min; the rate after 15

TABLE 22 - DEGRADATION OF POLYISOBUTENES AT 310°C.

Time	Pirani reading	Manometric volatile pressure	Extent of degradation	Rate of volatile production	Rate of degradation
min.	torr	cm.	%	mg./min.	%/min.
Polymer F5(1)		W_o= 102.2mg.			
0	0.021	—	0	—	—
30	0.0092	1.890	12.5	0.168	0.424
60	0.0070	3.072	20.3	0.110	0.278
90	0.0066	4.111	27.2	0.100	0.252
120	0.0061	5.033	33.2	0.090	0.227
180	0.0053	6.625	43.8	0.073	0.184
240	0.0047	8.050	53.1	0.059	0.149
Polymer F4		W_o= 96.0mg.			
0	0.018	—	0	—	—
30	0.0074	1.505	10.5	0.120	0.322
60	0.0067	2.520	17.6	0.102	0.274
90	0.0060	3.420	23.9	0.088	0.236
120	0.0057	4.371	31.3	0.081	0.217
180	0.0045	5.588	39.1	0.055	0.147
250	0.0039	6.848	47.9	0.042	0.113
320	0.0034	8.110	57.1	0.034	0.091
Polymer F2, End groups chlorinated, W_o= 101.6mg.					
0	0.020	—	0	—	—
30	0.0069	1.695	11.2	0.108	0.274
60	0.0064	2.641	17.5	0.097	0.246
90	0.0060	3.561	23.6	0.088	0.223
120	0.0055	4.329	28.7	0.077	0.195
310	0.0038	8.250	54.7	0.040	0.101

TABLE 23 - DEGRADATION OF POLYISOBUTENES AT 310°C.

Time	Pirani reading	Manometric volatile pressure	Extent of degradation	Rate of volatile production	Rate of degradation
min.	torr	cm.	%	mg./min.	% /min.
Polymer IB4, W_o = 100.8 mg.					
0	0.022	—	0	—	—
30	0.0093	1.905	12.8	0.170	0.436
60	0.0071	2.964	19.9	0.112	0.287
90	0.0065	3.904	26.1	0.098	0.251
120	0.0060	4.840	32.4	0.088	0.226
180	0.0052	6.175	41.3	0.071	0.182
240	0.0049	7.816	52.2	0.064	0.164
302	0.0040	9.100	60.8	0.044	0.113
350	0.0032	9.755	65.3	0.034	0.087
400	0.0028	10.327	69.1	0.026	0.067
∞	10^{-4}	14.950	100.0	0	0
Polymer F1, W_o = 100.0 mg.					
0	0.021	—	0	—	—
15	0.0125	1.294	8.69	0.240	0.620
45	0.0075	2.667	17.9	0.122	0.315
80	0.0066	3.880	26.1	0.100	0.258
120	0.0060	5.204	35.0	0.088	0.227
160	0.0053	6.248	42.0	0.073	0.188
220	0.0044	7.529	50.6	0.053	0.137
300	0.0035	9.082	61.0	0.035	0.090
400	0.0030	9.550	64.2	0.028	0.072
∞	10^{-4}	14.883	100.0	0	0

TABLE 24 - DEGRADATION OF POLYISOBUTENES AT 310°C.

Time min.	Pirani reading torr	Manometric volatile pressure cm.	Extent of degradation %	Rate of volatile production mg./min.	Rate of degradation % /min.
Polymer F5, End groups chlorinated, W_o = 100mg.					
0	0.027	—	0	—	—
30	0.0093	—	—	0.170	0.438
60	0.0072	3.398	22.8	0.115	0.296
120	0.0050	4.910	33.2	0.066	0.170
180	0.0043	6.149	41.3	0.050	0.129
240	0.0036	7.171	48.2	0.037	0.095
300	0.0033	8.112	54.5	0.033	0.085
Polymer F5(2), W_o = 100.6 mg.					
0	0.018	—	0	—	—
30	0.0090	1.330	9.0	0.162	0.415
60	0.0074	2.502	17.0	0.120	0.308
120	0.0059	4.536	30.7	0.085	0.218
180	0.0047	5.961	40.4	0.059	0.151
300	0.0036	7.582	51.4	0.037	0.095

FIGURE 30. RATE CURVES FOR POLYISOBUTENE DEGRADATION AT 310°C.

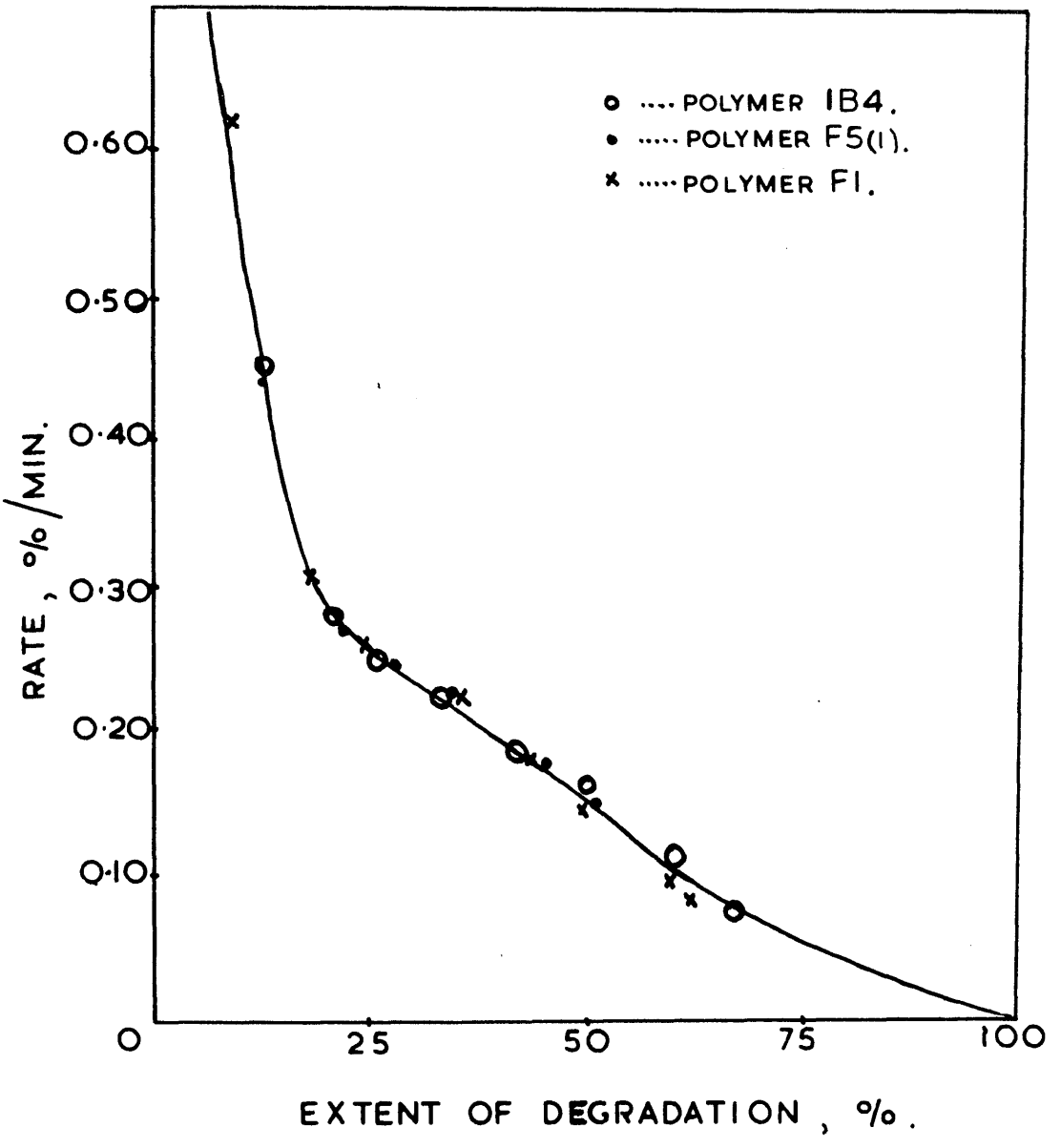


FIGURE 31. RATE CURVES FOR POLYISOBUTENE DEGRADATION AT 310°C.

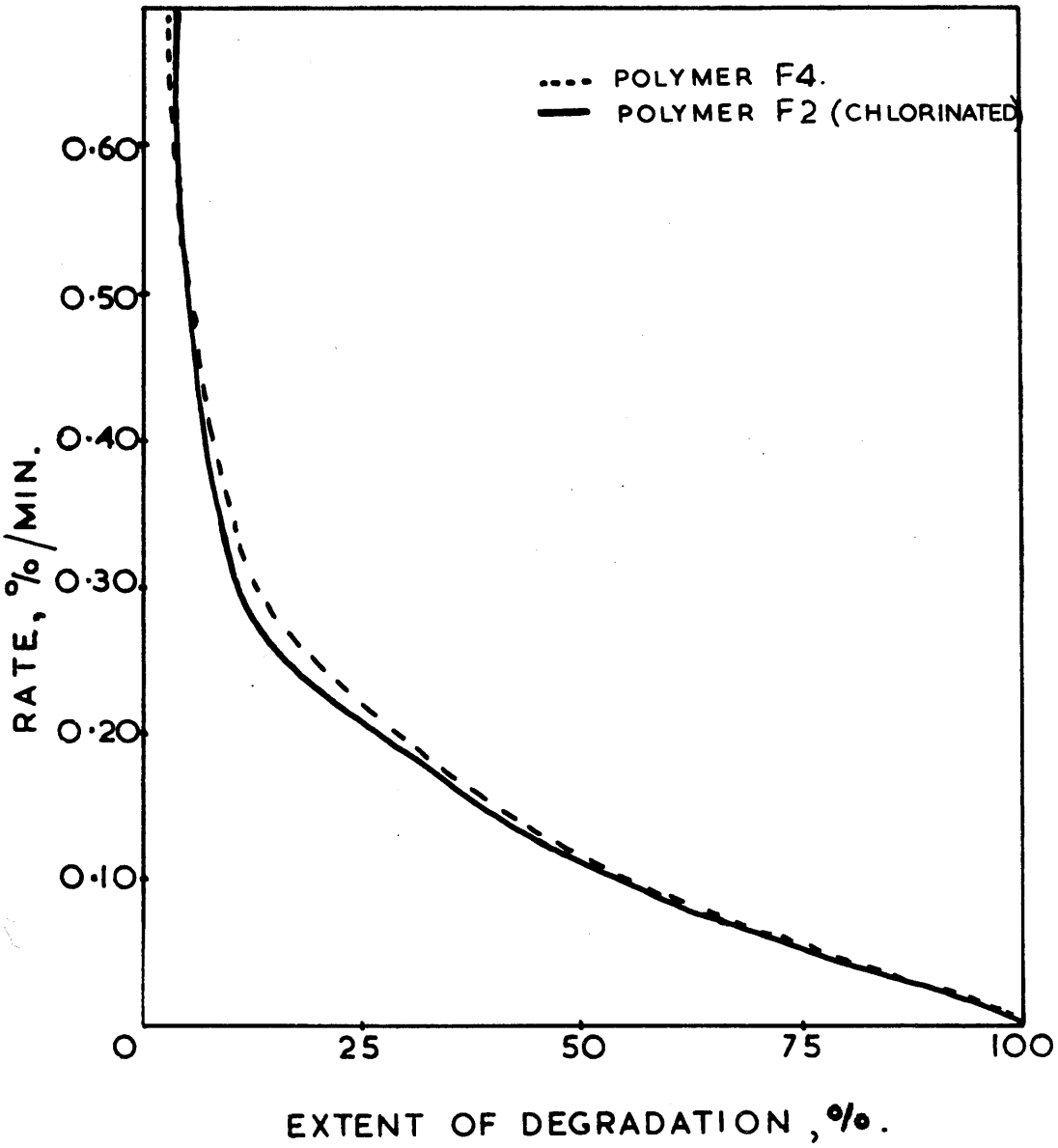
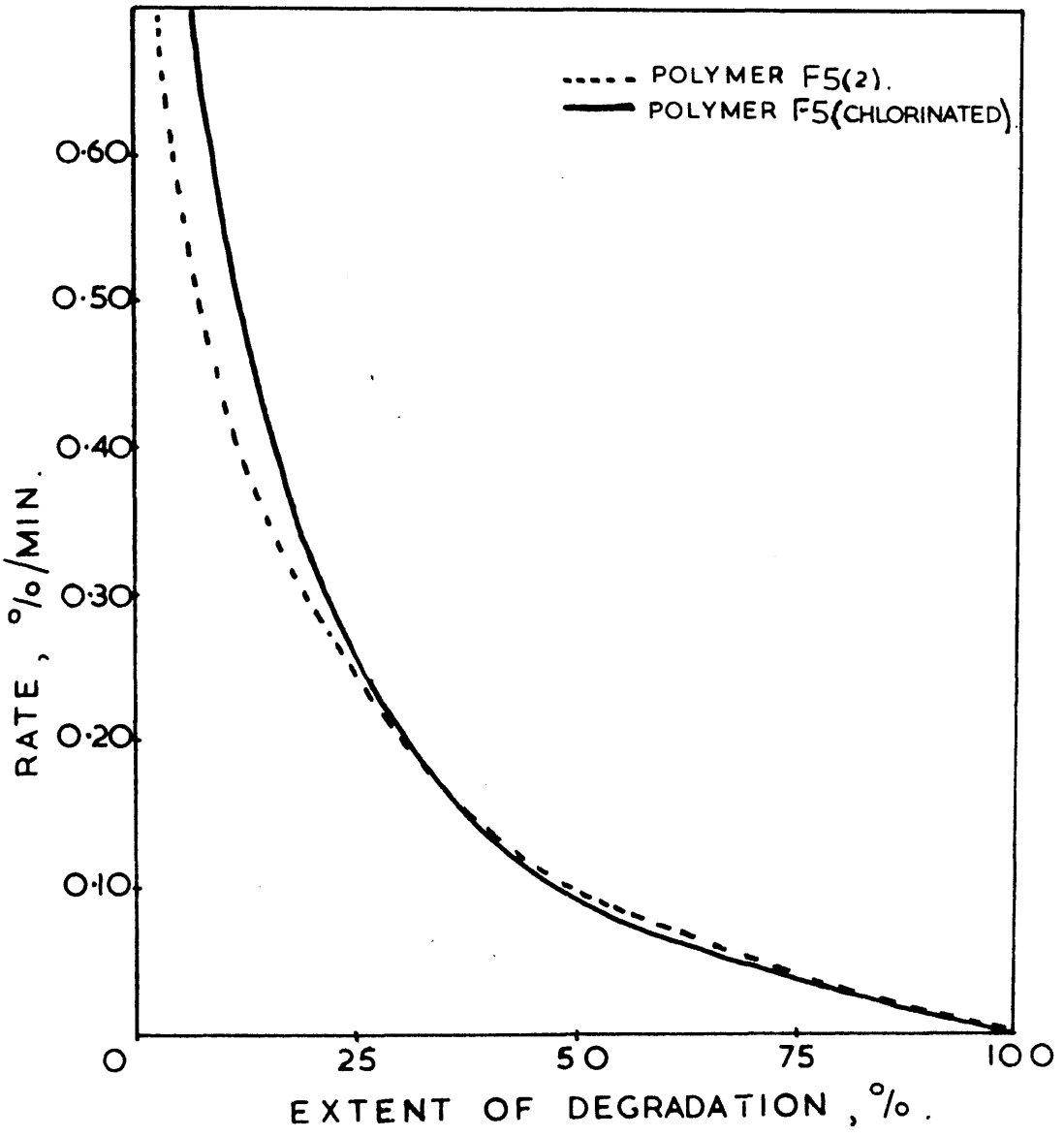


FIGURE 32. RATE CURVES FOR POLYISOBUTENE DEGRADATION AT 310°C.



minutes derived from the pirani pressure was 0.62%/min. The rates derived from % degradation values were also concluded to be in error. In this case the results tend to be lower than the true rates in the early stages of the curves (figure 33). Since the fall in rate is not linear with respect to time the mean rate is the same as the true rate only when the time interval is very small. The errors produced by this method should not however be large so that the true rate curve probably lies closer to curve (2) in figure 33 than to curve (1).

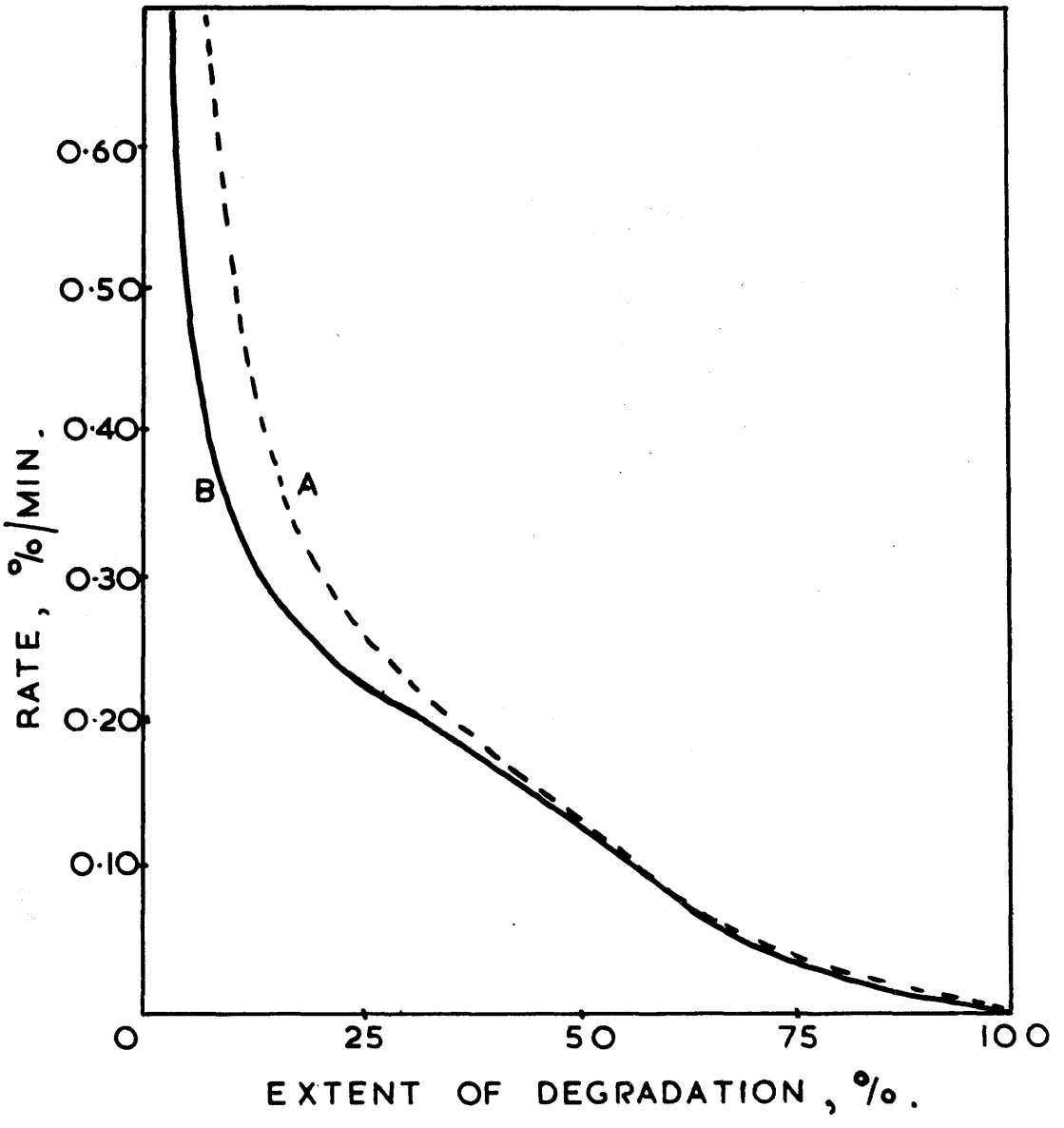
TABLE 25. RATES OF DEGRADATION FOR POLYMER F1 FROM % DEGRADATION - TIME DATA.

Time min.	Extent of Degradation %	Rate of Degradation %Deg./min.	Rate of Degradation mg./min/100mg.residue.
15	8.7	0.400	0.438
45	17.9	0.255	0.310
80	26.1	0.230	0.311
120	35.0	0.205	0.316
160	42.0	0.175	0.301
220	50.6	0.137	0.278
300	61.0	0.090	0.228
400	64.2	0.072	0.202

FIGURE 33. COMPARISON OF RATE CURVES DERIVED FROM:

A - PIRANI MEASUREMENTS.

B - % DEGRADATION - TIME DATA.

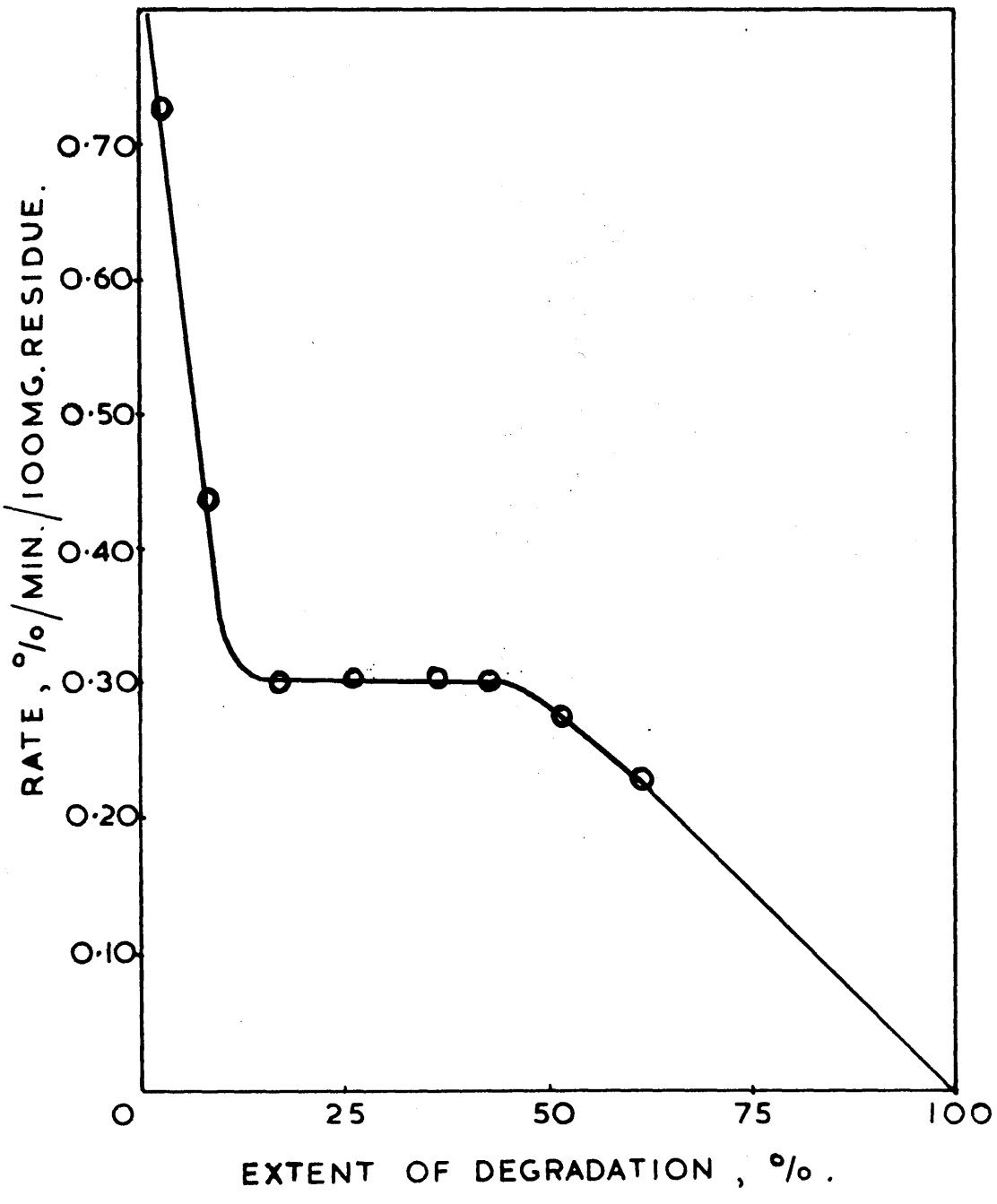


Comparison of the rate curves for polymers of different molecular weight showed that the initial rate of degradation was independent of molecular weight. The curves could be divided into a sharp initial fall in rate followed by a more gradual decrease. Since the decreasing weight of sample could be responsible for the decrease in rate with extent of degradation, the rates in % per minute were converted into rates in the units, % per minute per 100 mg. residue. Rates defined in this way are given in table 25 for polymer F1. Figure 34 shows the shape of the rate curve derived from the data in this table. The initial fall in rate was still evident. The rate became constant after 15% degradation and a plateau region was observed. The rate decreased again after 50% degradation. These deviations from the horizontal line predicted from theory[92] were concluded to result from; (a) additional degradation reactions at beginning of degradation and (b) distillation of low molecular weight polymer instead of degradation during latter stages; this causes the "tailing-off" effect observed in the rate curve.

EFFECT OF DEGRADATION ON MOLECULAR WEIGHT.

Residues of polymer F1 degraded at 310^{o}C were dissolved in toluene and the molecular weights measured in the

FIGURE 34. RATE CURVE FOR POLYMER F1;
RATE AS FUNCTION OF RESIDUE WEIGHT.



osmometer. The results are given in table 26. The lowest molecular weight residue showed signs of diffusion in the osmometer so that the figure shown was an approximate estimate. The sharp fall in the molecular weight is illustrated in figure 35; the M.W. dropped to 10% of its original value after 2.5% degradation, but thereafter decreased slowly.

The numbers of bonds broken per molecule were derived from the molecular weights of the residues using the equation,[3]

$$n = \frac{p_o}{p_t} - 1$$

where n is the number of bonds broken per molecule,

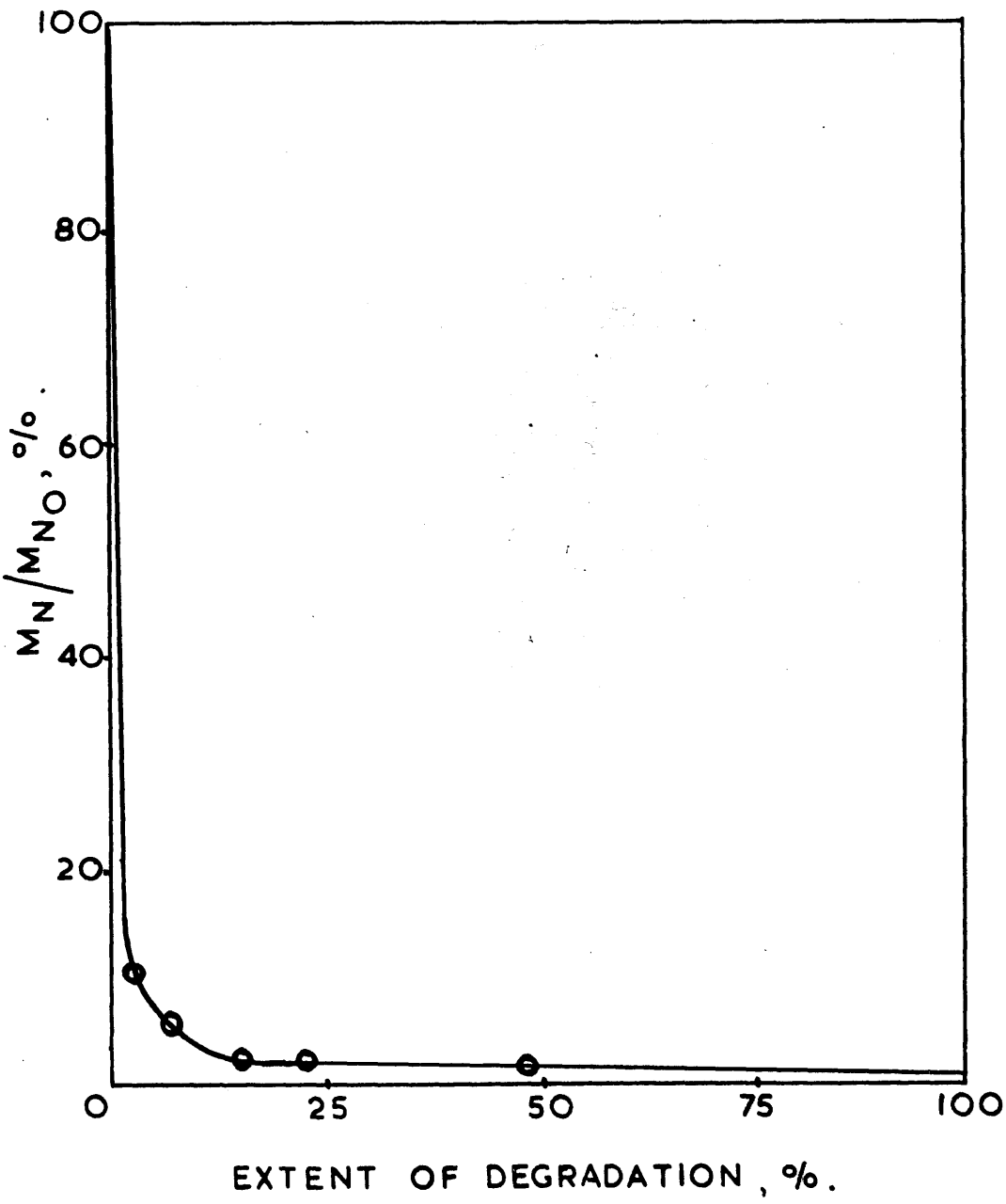
p_t is the chain length, $\frac{M_n}{M_1}$, at time, t,

and p_o is the original chain length.

TABLE 26. EFFECT OF DEGRADATION ON M.W. OF RESIDUE.

Time of degradation min.	Extent %	M_n of residue	$\frac{M_n}{(M_n)_o}$	Bonds broken per molecule
0	0	376,000	1	0
10	2.5	39,400	0.105	8.55
30	7.0	18,100	0.048	19.8
50	14.5	11,400	0.030	32.3
70	22.0	9,300	0.025	39.0
210	49.0	(6,000)	(0.016)	(61.5)

FIGURE 35. DEPENDENCE OF MOLECULAR WEIGHT ON EXTENT OF DEGRADATION.



The changes in the number of bonds broken with time and extent of degradation are shown in figure 36. It appears that neither relationship is linear which is consistent with the rate characteristics previously presented i.e. these results also reflect an initial rapid decrease in the rate of degradation.

The rate data obtained by the pressure method and the M.W. changes were combined by computing the rate per g. residue as a function of the reciprocal chain length. The result is shown in figure 37. The theoretical lines for different degradation behaviours are also indicated in this figure.[93] In end-initiated degradation, the rate of degradation is proportional to the number of chain ends in the sample and therefore inversely proportional to the molecular weight of the sample. When a random initiation mechanism operates the rate of initiation is independent of the molecular weight of the sample so that the rate vs. $^{1}/_{P}$ curve is predicted to be a horizontal line. The experimental data were observed to follow approximately the random case after the initial stages of degradation, in which a rapid decrease in rate was once more evident.

FIGURE 36. NUMBER OF CHAIN SCISSIONS AS FUNCTION OF TIME AND EXTENT OF DEGRADATION.

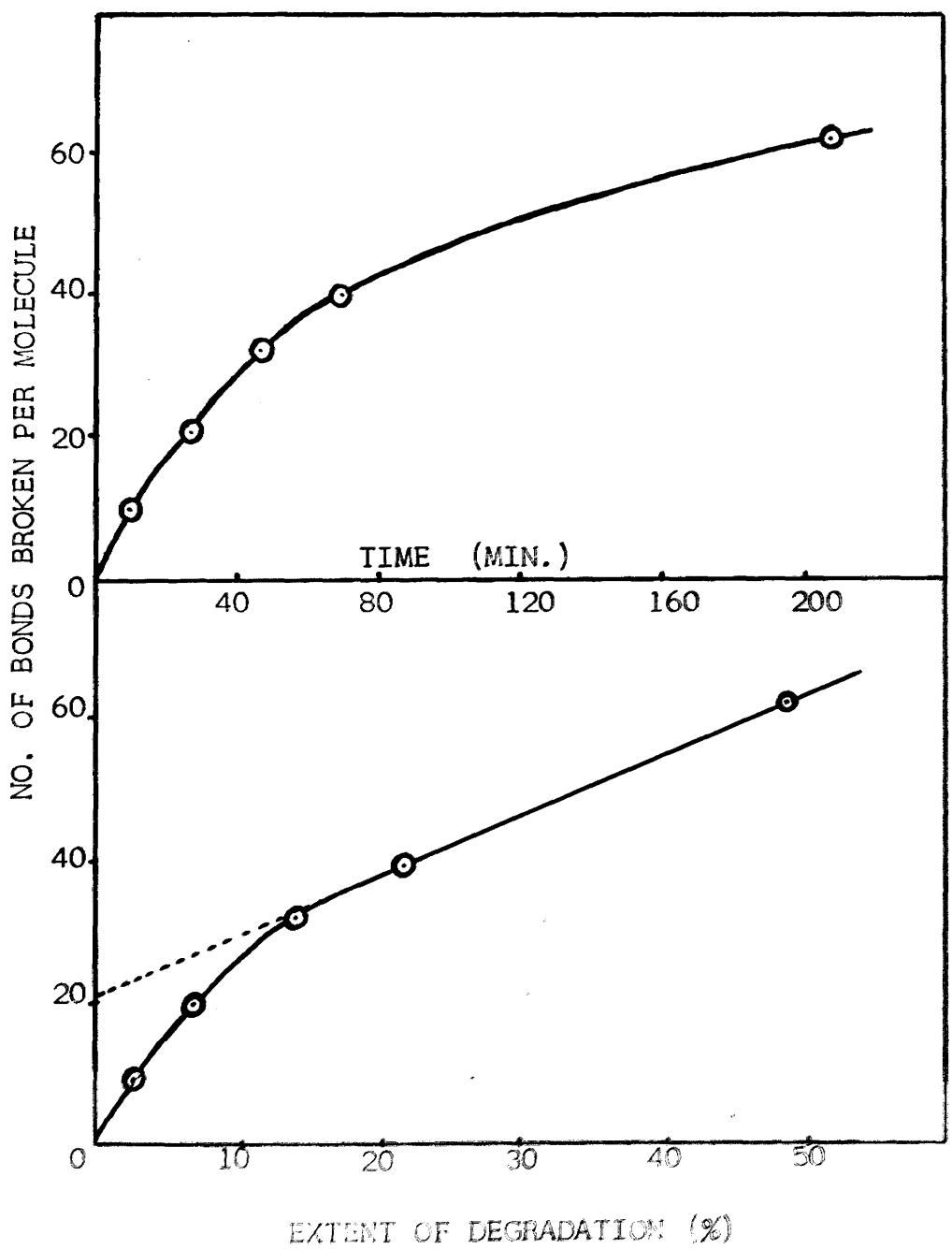
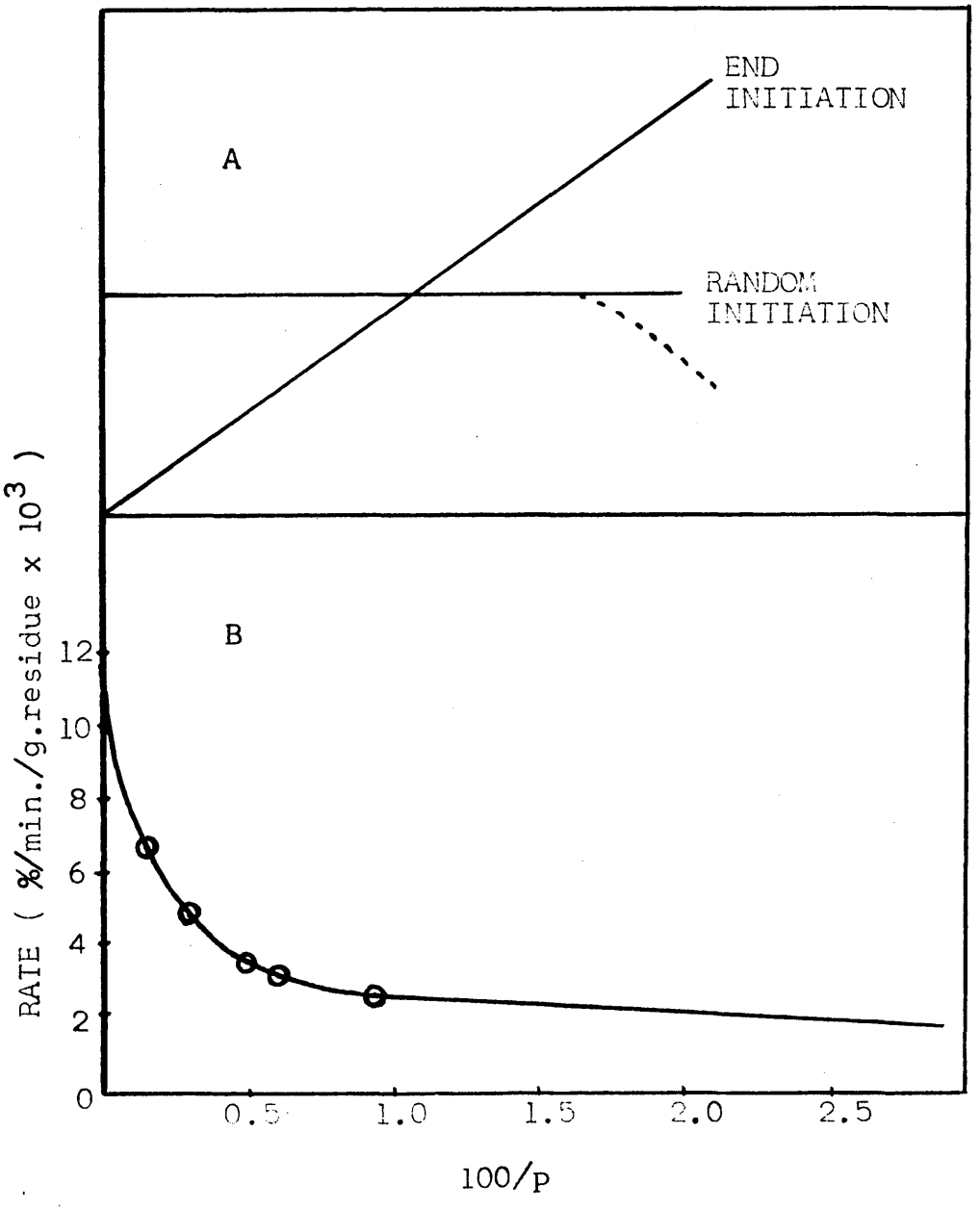


FIGURE 37. DEPENDENCE OF RATE OF DEGRADATION ON CHAIN LENGTH OF RESIDUE:

A - THEORETICAL LINES.[43]

B - EXPERIMENTAL CURVE FOR POLYMER F1.



PRODUCTS OF DEGRADATION.

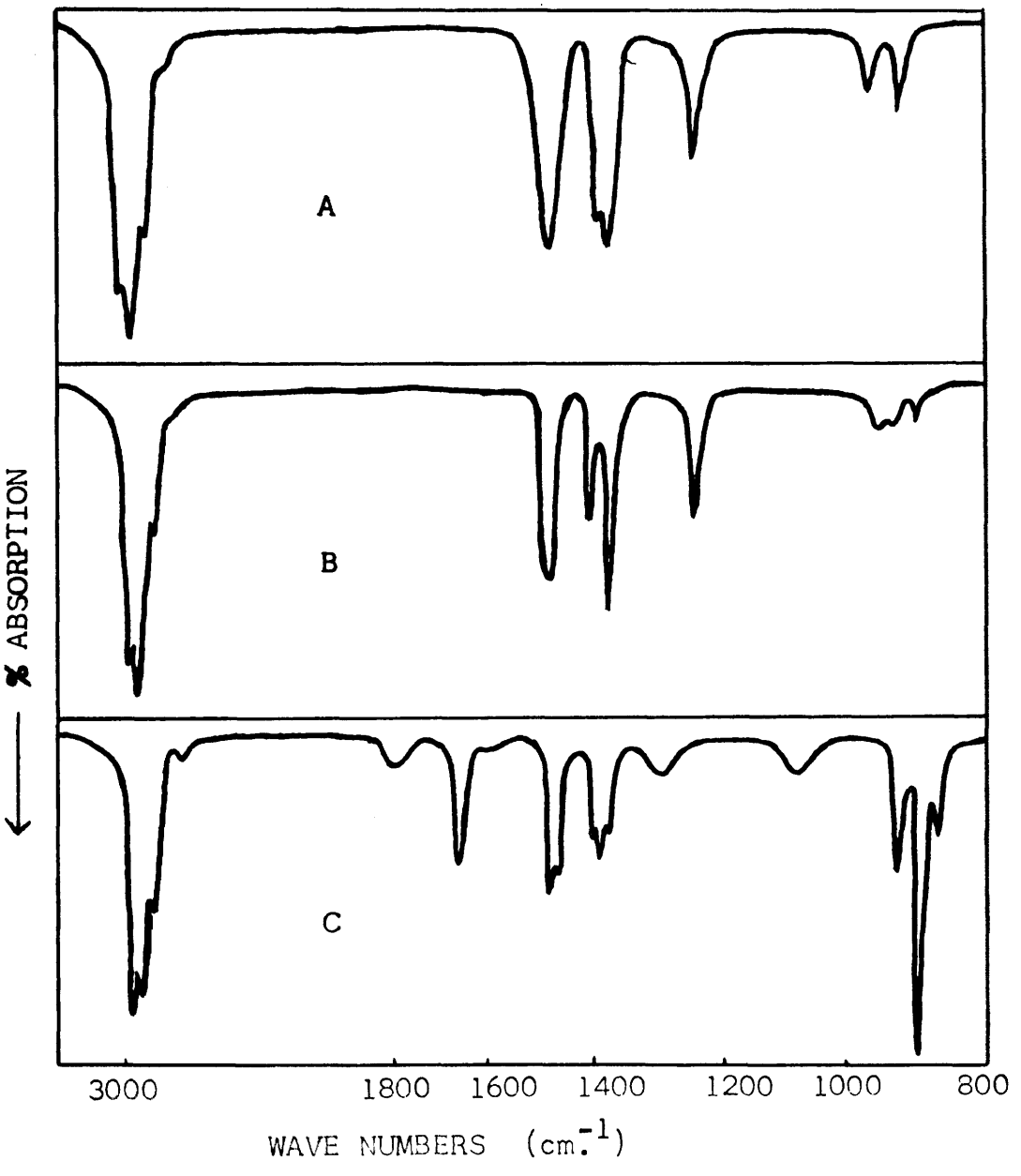
Since the products of polyisobutene degradation have been thoroughly investigated,[54,70,94-97] further detailed examination was considered superfluous. It was confirmed, however, that the products were qualitatively similar to those found by previous workers. The distribution of volatile to cold-ring fraction was approximately 40:60, which is comparable to the V_{25} : V_{pyr} ratio of 30:70 found by Madorsky.[54] Figure 38 shows the I.R. spectra (P.E. 237 instrument) of the polymer and cold-ring fraction (10% CCl_4 solutions), and the gas spectrum of the volatiles (10cm. gas cell, Research and Industrial Instruments Co.). Detailed analysis of the volatile fraction was not carried out, but the significant presence of dimer was confirmed by mass spectrometry which showed a peak at m/e ratio = 112. The cold-ring fraction had a similar I.R. spectrum to the parent polymer and consisted of low M.W. polyisobutene. The molecular weight was measured by vapour-phase osmometry[98] (Mechrolab vapour phase osmometer, model 301A) and found to be of the order of 500-1000.

FIGURE 38. I.R. SPECTRA:

A - POLYISOBUTENE.

B - COLD-RING FRACTION.

C - VOLATILE PRODUCTS.



DISCUSSION.

The experimental results obtained from weight-loss studies were in qualitative agreement with those published by Madorsky.[38,54] The rates in the present study were about 70% of the values found by Madorsky for equivalent temperatures. A similar discrepancy was found by McIntyre, O'Hara and Straus[55] whose rates were approximately 50% of Madorsky's values. The observed value of the activation energy, 52 k.cal.mole^{-1}, was in better agreement with the values of 49 and 52 k.cal.mole^{-1} reported by Madorsky than with the lower value of 41 k.cal.mole^{-1} found by Inoue, Ouchi and Yasuhira.[99] The activation energy is consistent with the scission of a carbon-carbon bond at a quaternary carbon atom; for cleavage at tertiary carbon atoms as in polypropylene[38,100] and secondary carbon atoms in polyethylene[101,102] the respective activation energies of 55-58 k.cal.mole^{-1} and 60-64 k.cal.mole^{-1} have been observed.

Several facets of the work clearly indicate that initiation consists of random scission of the polymer chains, and that, although the polyisobutene chains have unsaturated ends, terminal initiation is unimportant. The predominance of random cleavage is shown by the sharp

decrease in the molecular weight of the polymer during the initial stages of degradation. The shape of this curve, which is illustrated in figure 35 is characteristic of a random process[103]. Further evidence of the absence of end initiation is presented in figure 37 in which the experimental results are compared to theoretical lines for random and terminal initiation. A final proof is obtained from the rate studies of fractionated polymers. If end initiation was prevalent the initial rate of degradation would be proportional to the number of chain ends present in the sample, and therefore inversely proportional to the molecular weight of the starting material.[39] For polyisobutene, no such molecular weight effect was observed.

The nature of the primary radical formed has been the subject of considerable speculation. By degrading polyisobutene in the presence of additives, Thomas[104] concluded that scission of the carbon chain was the initial reaction. An alternative mechanism has been proposed by Dolgoplask et.al.[105] in which the primary reaction consists of abstraction of a hydrogen atom from the chain. It is significant that in the radiolysis of polyisobutene both hydrogen abstraction and carbon-carbon bond scission were again postulated[106,107] but recent work

by Turner[108] supports the direct fracture of the polymer chain.

The extent of depropagation and transfer reactions is ascertained from the nature of the degradation products (page 148). Reference has been previously made to the mass-spectrometric investigation by Madorsky and co-workers,[54,96] in which the monomer yield constituted 18% by weight of the total products. A similar product distribution was obtained by Barrel, Porter and Johnson[94] using G.L.C. techniques. Slobodin and Matusevich[70] concluded that the degradation products consisted of 51% C_4, 17% C_8, 18% C_{12}, and 14% heavier fragments. An even higher monomer yield (78%) was reported by Wall[95] and, in complete contrast, a negligible monomer yield was observed by Golubtsova.[97] The variation in product distribution can be attributed to differences in the preparative details of the polyisobutenes studied. Since the monomer yield is higher than for a completely random degradation and considerable quantities of dimer and trimer are formed, it is evident that both unzipping to monomer and intramolecular transfer are important in this degradation. That intramolecular transfer supersedes intermolecular transfer is supported by the observed M.W. changes. The drop in M.W., 10.5%, after 2.5% degradation was much less drastic than that

observed for polyethylene[109] in which intermolecular transfer becomes more important.

The deviations from a true random process are responsible for the shape of the rate curves which were strikingly different from the type of curve predicted by random theory.[42-44] According to this theory the rate should build up from zero to a broad maximum at approximately 25% conversion. The observed rate curves fell sharply from a initially high value, levelled out, and dropped gradually to zero at complete degradation. The absence of the predicted rate maximum in certain other polyolefins permits a feasible analogy to be made. Thus certain ethylene and propylene polymers exhibited rate curves which decreased continuously from an initial high value.[109] Wall and Straus[110] have explained this phenomenon in terms of branching and they showed that linear polyethylene and polypropylene did in fact conform to the random theory. The effect of branching was to introduce initial cleavage sites, and, providing the branches were longer than methyl groups, steric effects inhibited intermolecular transfer. In polyisobutene the twin methyl groups apparently produce the same effect and intramolecular transfer is favoured. Curves showing the time dependence of bond scission for polyethylene[4] and polypropylene[111] are qualitatively similar to the

experimental curve for polyisobutene which is presented in figure 36. MacCallum[112] has reviewed this treatment for several polymers and in certain cases the curves can be interpreted in terms of weak links which aid other scission processes in the initial stages of degradation. It is plausible therefore that weak links are also present in polyisobutene.

The rapid decrease in rate during the early stages of degradation, which has been consistently observed in the present study, was not found in a similar investigation by McIntyre et.al.[55] for polymers of M.W.>50,000. Higher initial rates found by these workers for very low M.W. polymers were attributed to the presence of appreciable amounts of oligomeric material which could distil directly from the system without degradation. This explanation seems unreasonable in the present study in which polymers of M.W. 30,000 - 400,000 were studied, cf. figures 34 and 37. The discrepancy between McIntyre's results and the present work may be accounted for by differences in polymer structure, e.g. labile structures resulting from the incorporation of impurities during polymerisation, or, alternatively, on the basis that the high initial rates would be less likely to be detected in McIntyre's apparatus in which the polymer took 15 minutes to reach the temperature of degradation; it was within this interval

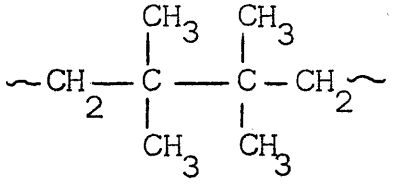
that the present study, in which the polymer sample could be heated more rapidly [Chapter 2, sect.3(iv)], revealed the rapid decrease in rate.

CONCLUSION.

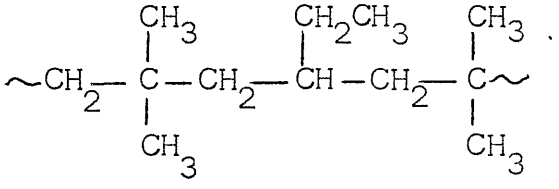
The observed rate characteristics can be explained in relation to two major effects which produce deviations from random theory.

a) Normal random initiation is supplemented by scission of labile bonds or weak links during the early stages of degradation. Possible weak links are,

1. Head to head linkages:



2. Longer branches than methyl groups which would arise if small quantities of but-1-ene for example were present in the isobutene used to prepare the polymer.



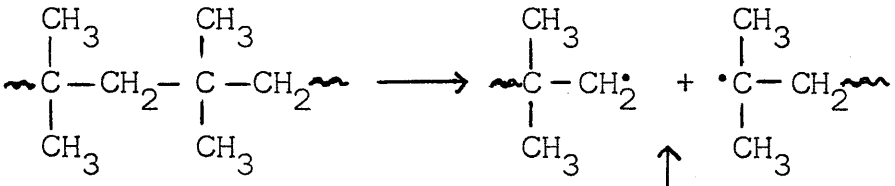
3. Abnormal structures produced by impurities during polymerisation.

(b) Further non-random behaviour is produced by the predominance of intramolecular transfer which not only increases the rate initially but influences the product distribution.

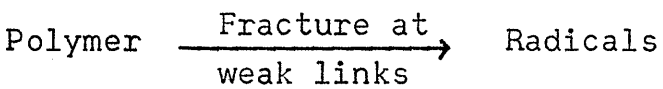
The mechanism of polyisobutene degradation can be represented by the following reaction scheme:-

Initiation:

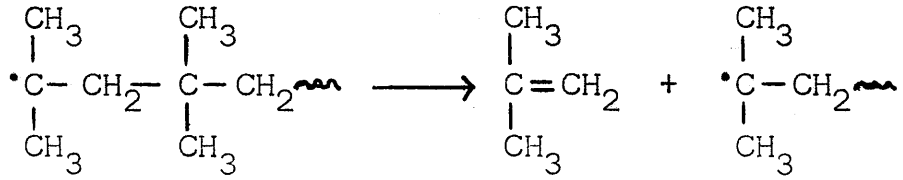
a) Normal:



b) Abnormal:



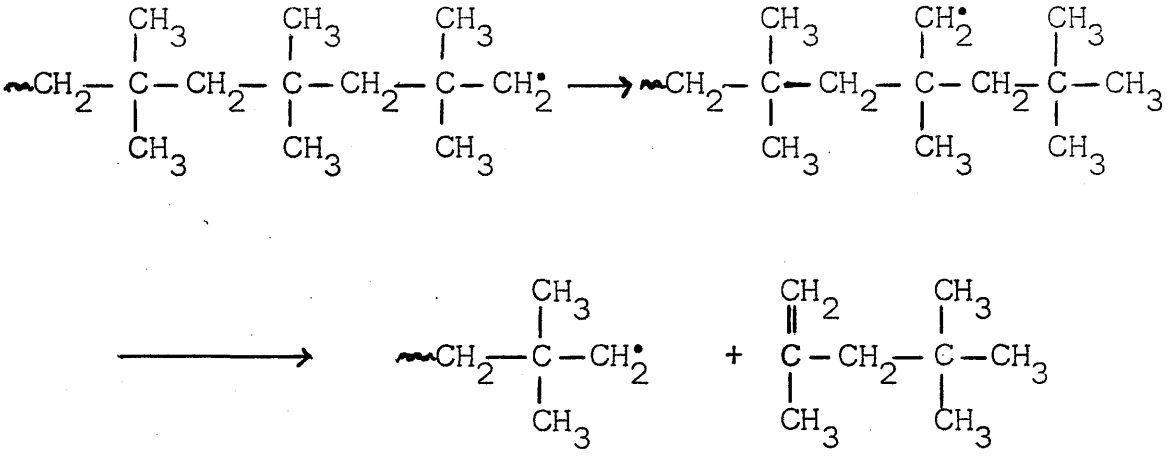
Depropagation:



(Monomer)

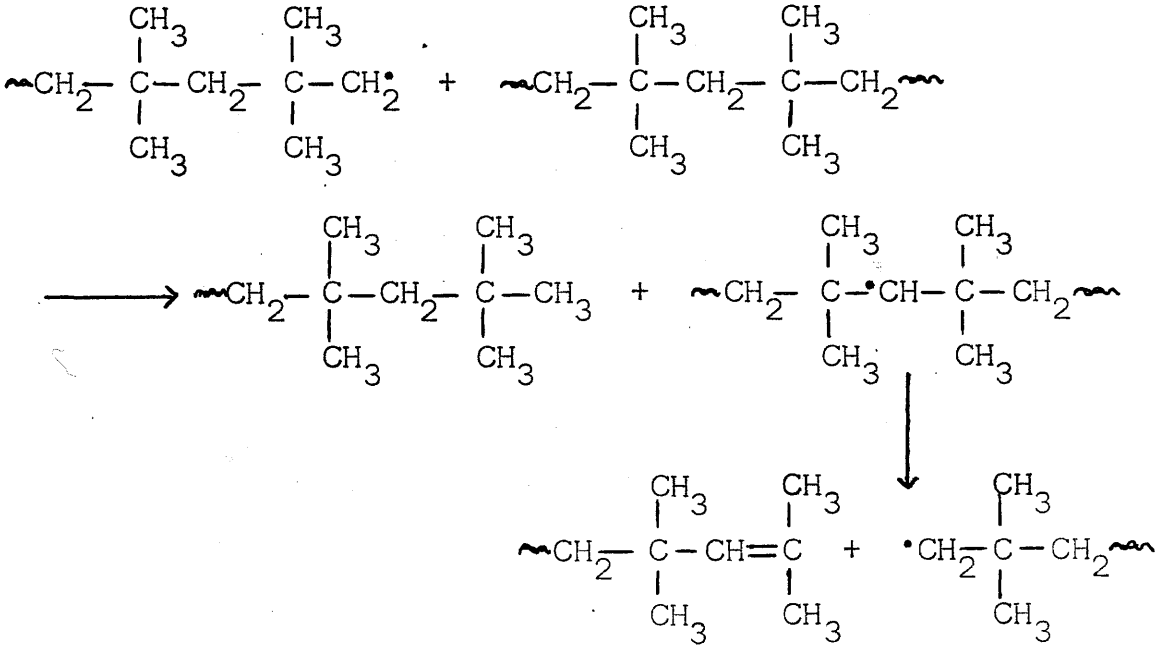
Transfer: (a) > (b)

(a) Intramolecular:



(Dimer, Trimer, etc.)

(b) Intermolecular:



CHAPTER 5.

PRELIMINARY STUDIES OF CHLORINATED POLYISOBUTENE.

It was noted in Chapter 4 that minute amounts of chlorine in polyisobutene, as in the case of end-group chlorinated polymers, produced a marked decrease in the thermal stability of the polymer. This is undoubtedly caused by the relative weakness of the carbon-chlorine bond which splits at a lower temperature and initiates the free-radical degradation reactions. In this chapter, the effect of much higher concentrations of chlorine in the polymer are examined.

MAIN-CHAIN CHLORINATION OF POLYISOBUTENE.

The method of chlorination has been previously described in Chapter 2, section 2, (ix); the extent of chlorination was varied by using different relative concentrations of polymer IB4 and chlorine in the reaction mixture, and the chlorine content of the product was measured radiochemically. The chlorination conditions and results for some preliminary chlorinations are listed in table 27. A curve was constructed which related the

TABLE 27. CHLORINATION OF POLYISOBUTENE MAIN-CHAIN AT 60°C.

Experiment reference	Wt. Polymer in reaction mixture mg.	Wt.% Cl	Initiator concentration mg.	Wt.% Cl in product
P1	202.5	13.73	2.0	9.68
P2	203.5	29.40	2.0	20.8
P3	120.0	50.16	0	35.1
P4	57.9	81.6	2.0	48.5
P5	12.9	94.7	0	46.0
P6	12.0	96.0	1.0	58.5
P7	11.0	88.2	0	72.3
P8	11.1	89.7	0.5	81.2
P9	46.2	85.3	0	63.8
P10	62.2	74.7	0	56.3
P11	50.6	69.3	0	55.5
P12	104.5	56.4	0	41.3
P13	98.6	49.7	0	29.4
P14	51.0	88.1	0	51.5
P15	469.2	1.95	0	0.185
P16	444.2	9.05	0	5.35
P17	289.3	36.0	0	24.0
P18	202.5	84.2	0	50.9

degree of chlorination of the polymer to the initial concentrations of reactants - figure 39. There was some scattering from the curve owing to slight differences in the experimental conditions of the chlorination. Using this relationship, the quantities of reactants were predetermined for the preparation of larger samples for degradation studies. The preparative details of these samples are given in table 28. It was observed that the chlorine contents of the polymers were usually higher than would have been predicted from the reaction of the given weights of chlorine and polymer by substitution i.e.

$$R\text{-}H + Cl_2 \longrightarrow R\text{-}Cl + HCl.$$

Since the chlorinated products were purified by reprecipitation, this feature was attributed to fractionation phenomena which resulted in the preferential precipitation of highly chlorinated chains. Thus polymer with low degrees of substitution did not precipitate well and tended to remain in solution. (cf. Chapter 2, section 2, (viii)).

It was often desirable to express the chlorine content of these derivatives as the average number of chlorine atoms per chain unit derived from the original monomer unit, rather than as a Wt.% Cl value. It is easily calculated

FIGURE 39. MAIN CHAIN CHLORINATION OF POLYISOBUTENE.

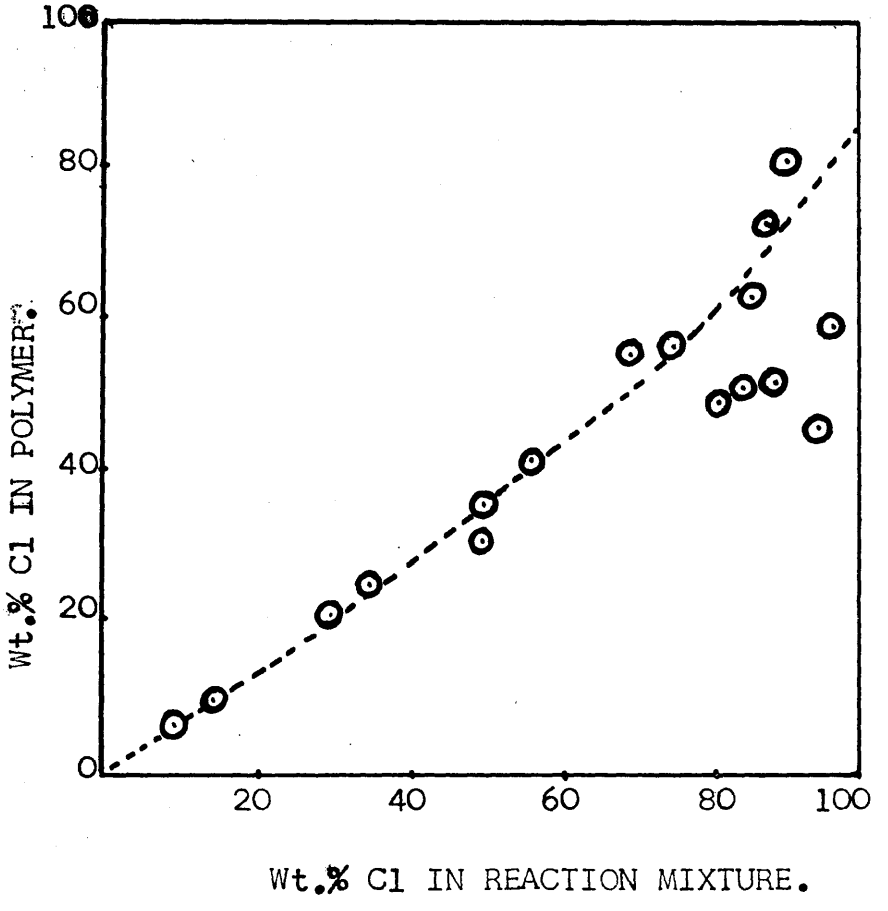


TABLE 28 - PREPARATION OF LARGER SAMPLES OF CHLORINATED POLYISOBUTENE.[a]

Reference	Wt. Polymer mg. in reaction mixture	Wt.% Cl	Wt.% Cl in product[b]	SA(GC)[c] cpm/mg.Cl
CD1	600	60	50.2	30.0
CD2	700	45	37.0	37.2
CD3	850	63	56.0	67.0
CD4	750	30	23.4	154.5

(a) The volume of the reaction mixture was increased to approximately 50 ml. in these preparations.

(b) The quantities of reactants used provided at least 1g. of chlorinated product.

(c) Other relevant specific activities were deduced from this value.

that the units, $-C_4H_7Cl-$, $-C_4H_6Cl_2-$, etc., correspond to Wt.% Cl values of 39.2 and 56.8, etc. Figure 40 shows the curve relating the two expressions; using this curve, the two units are readily interchangeable.

EFFECT OF CHLORINATION ON PHYSICAL PROPERTIES.

The first noticeable effect of chlorination was a gradual change in the physical form of the polymer as the degree of chlorination increased. The soft, rubber-like polyisobutene became tougher and fibrous in appearance at chlorine contents, 10 - 30%. At higher chlorine contents the product was hard and brittle, and could be readily powdered. Similar observations have been made in previous chlorinations of polyisobutene.[113,114]

The solubility of the polymer in various solvents was also dependent upon the degree of chlorination. Polyisobutene itself dissolves slowly in a number of organic solvents e.g. carbon tetrachloride, chloroform, hexane, toluene and benzene. The chlorinated derivatives tended to be less soluble in non-polar hydrocarbon solvents. Highly chlorinated derivatives were partly soluble in carbon tetrachloride and acetone, a non-solvent for the original polymer, and dissolved rapidly in chloroform. Chloroform was in fact the only common solvent which could be used as a solvent for

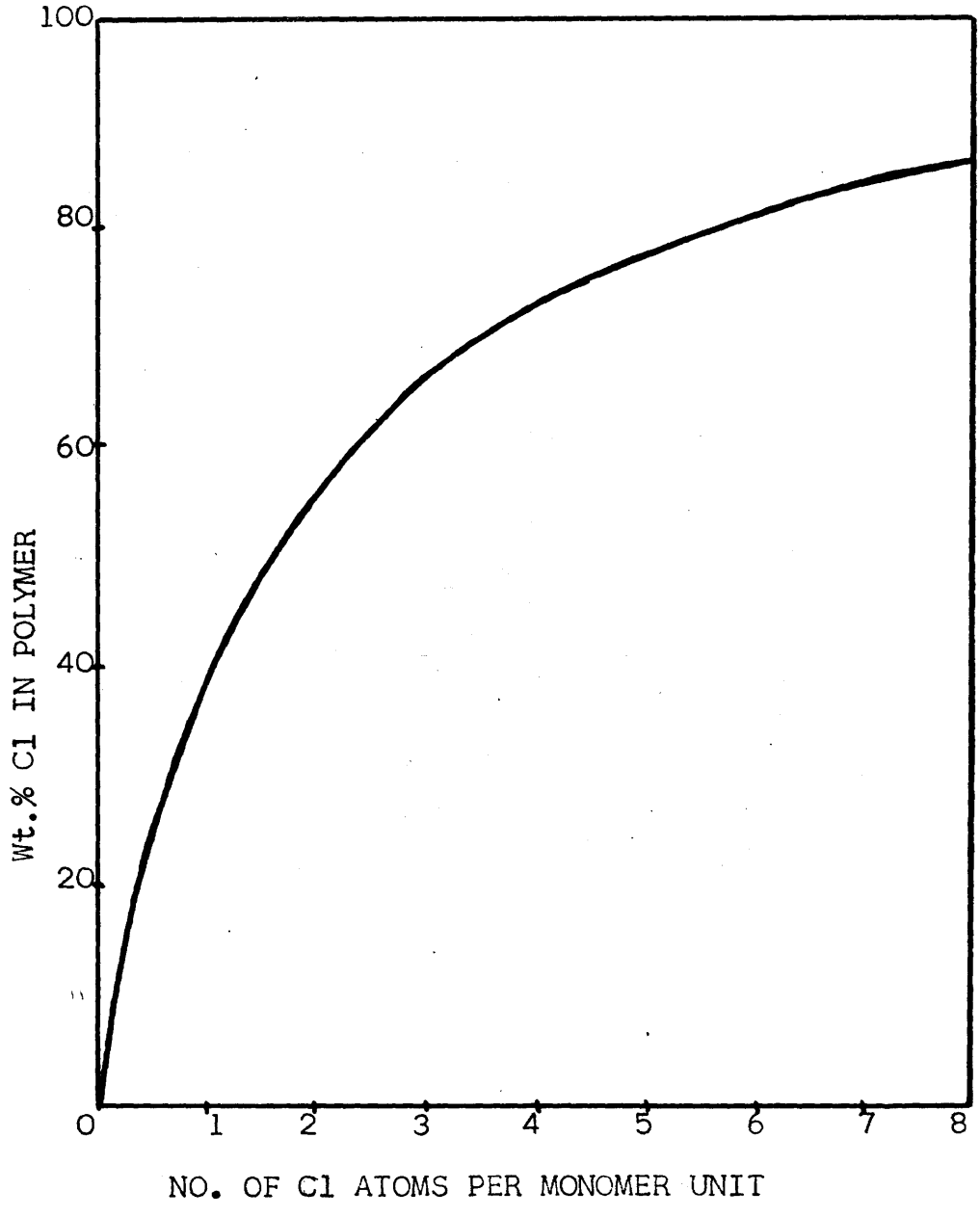


FIGURE 40. RELATIONSHIP BETWEEN Wt.%Cl IN POLYMER AND THE NUMBER OF CHLORINE ATOMS PER ORIGINAL MONOMER UNIT.

every chlorinated polymer.

The effect of chlorination on the molecular weight of polyisobutene is illustrated in figure 41 which was constructed from the data presented in table 29. Instead of rising as a result of hydrogen atoms being replaced by heavier chlorine atoms, the M.W. was observed to fall as the extent of chlorination increased. M.W. decreases have been observed in the chlorination of other polymers under similar conditions.[73,115] Since the chlorination proceeds by a free-radical substitution mechanism, it is accompanied by some chain scission reactions for which the following mechanism can be envisaged:

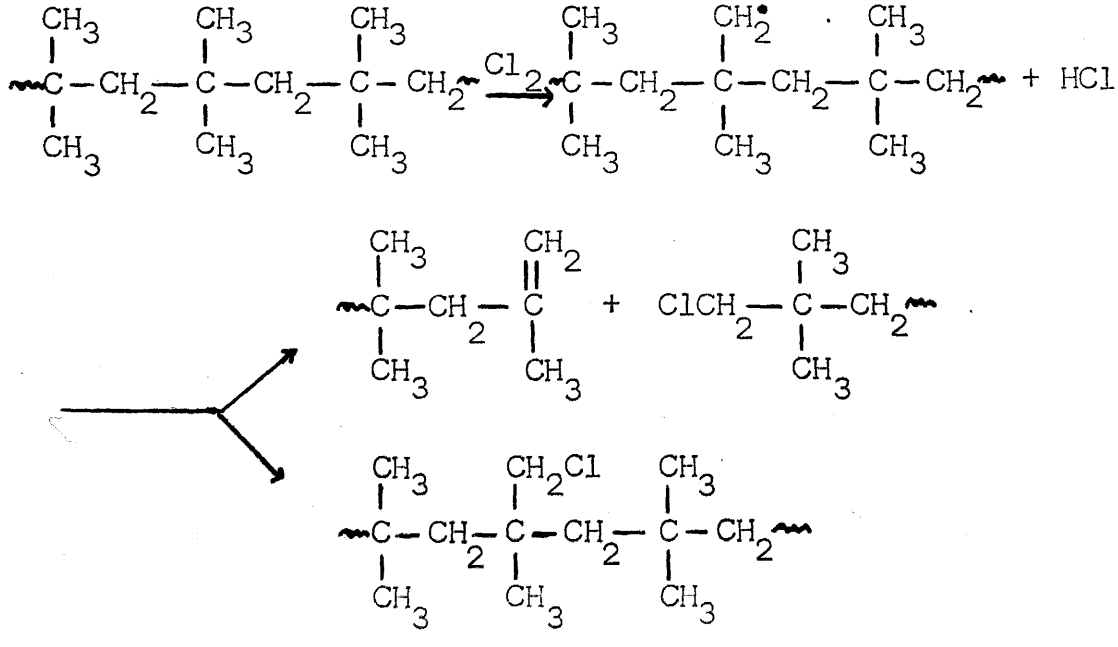


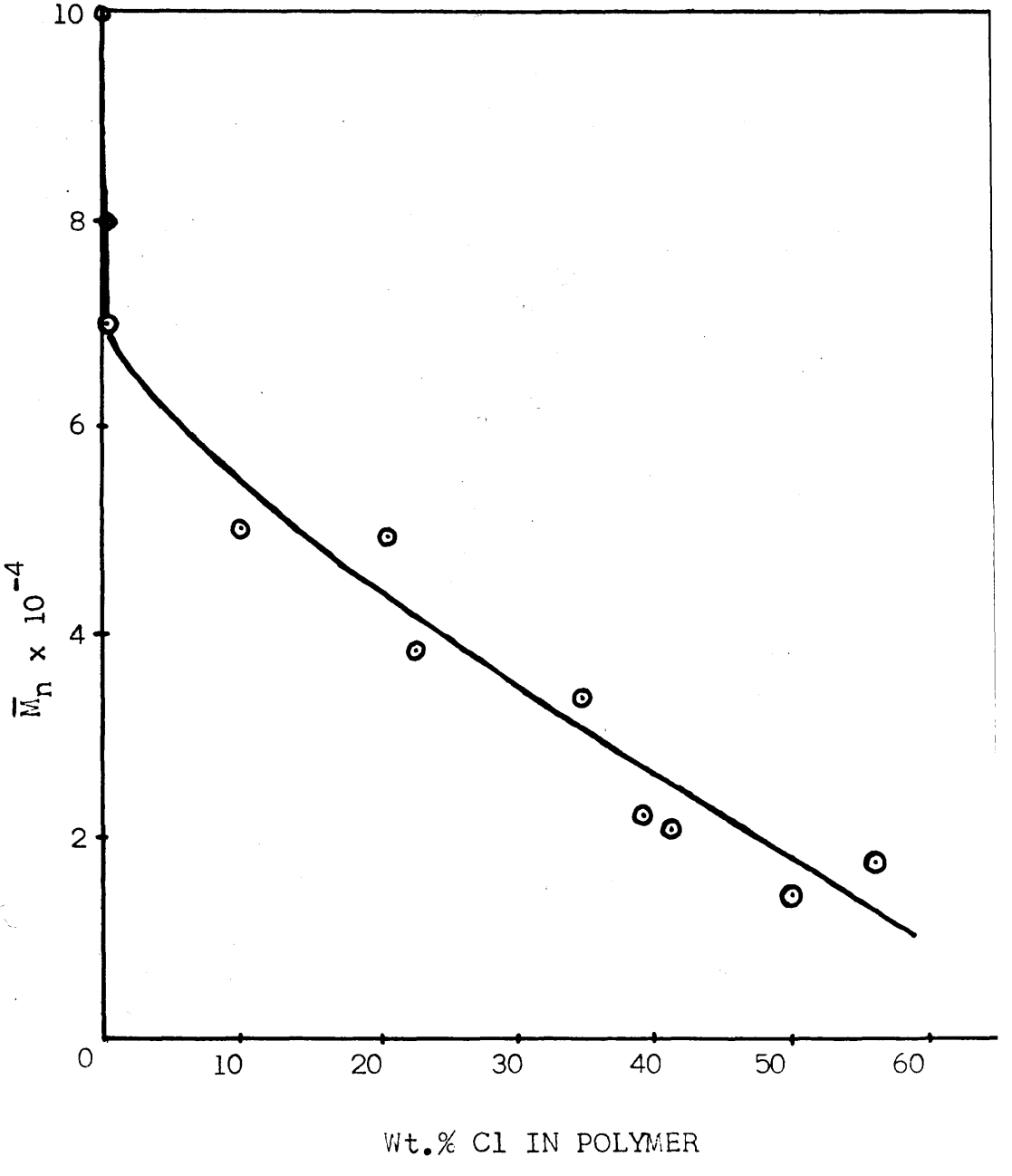
TABLE 29 - MOLECULAR WEIGHTS OF CHLORINATED POLYISOBUTENES.

Reference	Wt.% Cl in polymer	Molecular weight
P1	9.7	50,000
P2	20.8	49,000
P3	35.1	33,000
P12	41.3	20,000
CD1	50.2	12,700 (a)
CD2	37.0	22,000 (a)
CD3	56.0	17,000 (a)
CD4	23.4	38,000 (a)
S1	0.1	80,000 (b)
S2	0.2	70,000 (b)

(a) M.W. measured in $CHCl_3$ solution; other M.W. measurements were in toluene solution.

(b) The samples with reference S were low chlorinated derivatives prepared by chlorination at 50°C.

FIGURE 41. EFFECT OF CHLORINATION ON MOLECULAR WEIGHT.



STRUCTURE OF CHLORINATED POLYMERS.

I.R. SPECTRA.

I.R. techniques did not prove to be very useful in the elucidation of the structure of the chlorinated polymers. The difficulties of a systematic study were increased by the fact that no single method of sampling was applicable to the whole range of polymers. The spectra of two chlorinated polymers (KCl discs) are shown in figure 42, and can be compared to the spectrum of polyisobutene (figure 38). The presence of chlorine is shown by an intense band at $750cm^{-1}$ which in the spectra of highly chlorinated polymers becomes a broad band over the $700 - 900cm^{-1}$ region. A band also appears at $1290cm^{-1}$ corresponding to an overtone frequency of a C-Cl band outwith the spectrum. No significant decrease in the intensity of either the 1440 - 1470 band, (CH_2 and CH_3 groups), or the 1370 - 1390 band (CH_3groups), which would have indicated preferential substitution at the CH_3 or CH_2 groups, was observed.

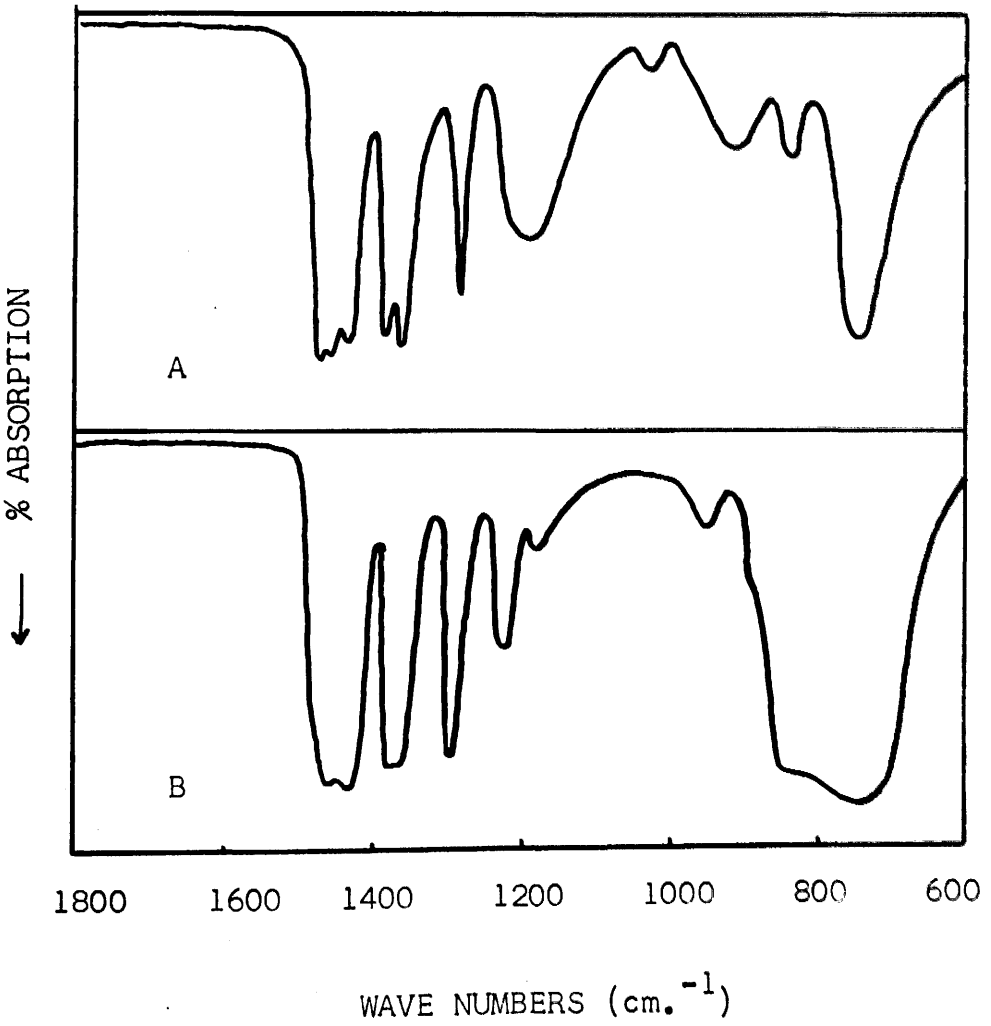
P.M.R. SPECTRA.

The use of P.M.R. techniques as an analytical tool in organic chemistry is well established.[116] Hydrogen nuclei

FIGURE 42. I.R. SPECTRA OF CHLORINATED POLYMERS:

A- POLYMER P13 - 30% Cl

B- POLYMER P10 - 56% Cl.



behave as small magnets in an applied magnetic field. The nuclei are distributed between two energy levels corresponding to different orientations of the magnetic moment. Transitions from one level to the other are brought about by the absorption or emission of electromagnetic radiation in the radiowave region. The ability of P.M.R. spectroscopy to distinguish different types of hydrogen atom, i.e. CH_3, CH_2, OH, CHO, etc., depends on a small but measurable effect known as chemical shift which splits the hydrogen atom absorption under high resolution. Chemical shifts arise from the screening of the nucleus by the electrons in its environment. Because of this shielding, the field experienced by the nucleus is slightly different from the applied field. As the screening increases the difference between the energy levels of the nucleus is reduced so that resonance absorption occurs at lower frequencies or higher external fields. Thus, chemically distinct environments give absorptions at slightly different applied fields and peaks are assigned τ values which are a measure of the shift relative to tetramethyl silane which has the highest shielding and is given the value $\tau = 10$.

$$\tau\,(\text{p.p.m.}) = 10 - 10^6 \frac{(H_{T.M.S.} - H_{obs.})}{H_{T.M.S.}}$$

Quantitative information can be obtained from the spectra since the intensity of the signal, or the area under the peak, is proportional to the number of hydrogen atoms in that environment. The ratio of peak areas is obtained by using the integrator of the spectrometer.

The application of P.M.R. spectroscopy to the study of polymer problems has become increasingly widespread in recent years. The straightforward analytical use is exemplified by the analysis of copolymer compositions,[117,118] whereas the elucidation of the stereochemistry and chain conformation of polymers illustrates a more elegant application.[119] P.M.R. techniques were used in the present study to establish the position of chlorine atoms in the polyisobutene chain. The similar but more complex problem of the structure of photochlorinated polymethyl methacrylate has been studied by Owens and Zimmerman.[120]

The study of chlorinated polymers by P.M.R. techniques proved very amenable since the restriction to chloroform as solvent did not present the same problem as in I.R. studies. Since chloroform was a suitable solvent, the polymers were studied as solutions in deuterochloroform which of course does not give any hydrogen atom absorption. The P.M.R. spectra of some chlorinated polymers are given in figures 43 and 44. In the spectrum of pure polyisobutene there were two peaks at 8.60 and 8.92 in the ratio 1:2.6

FIGURE 43. P.M.R. SPECTRA.

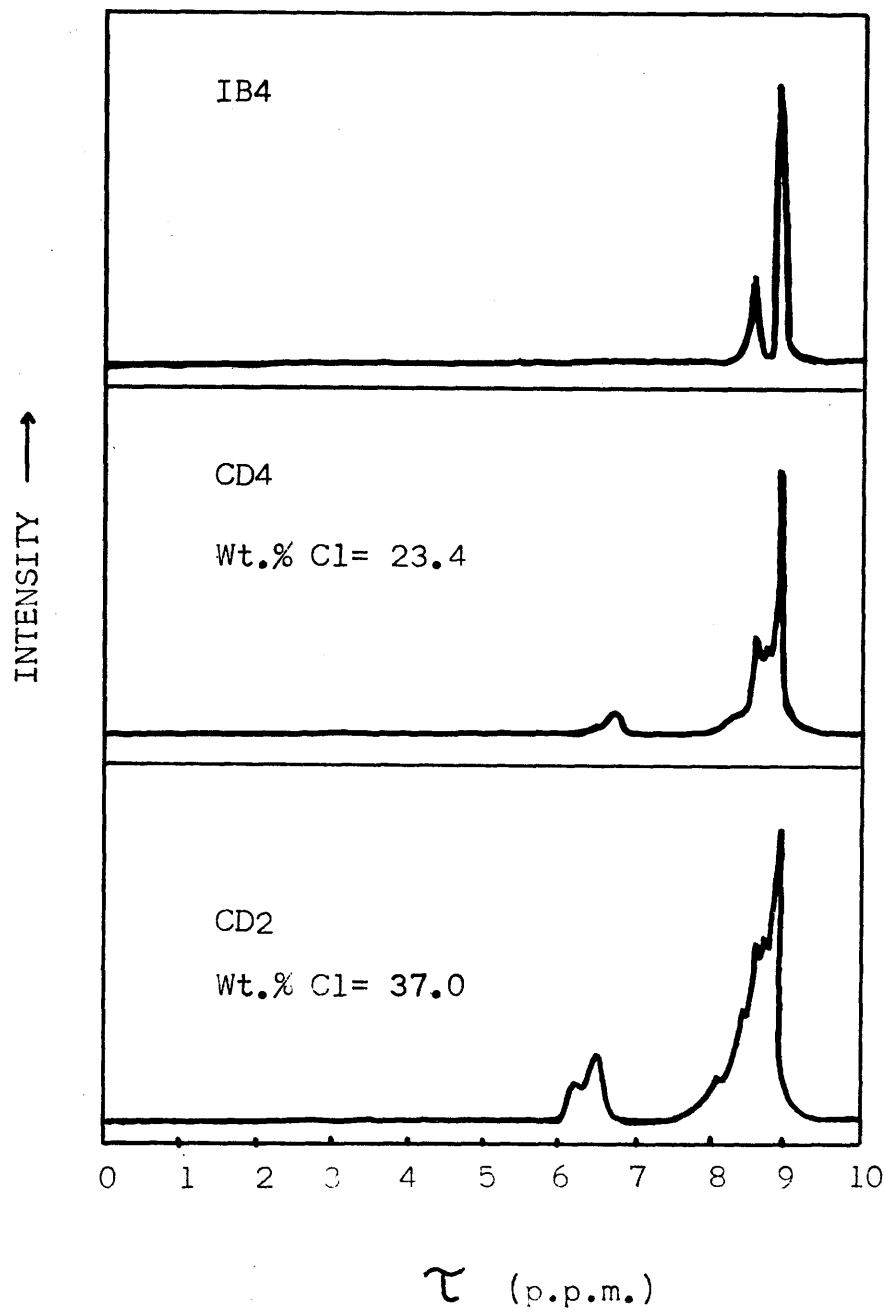
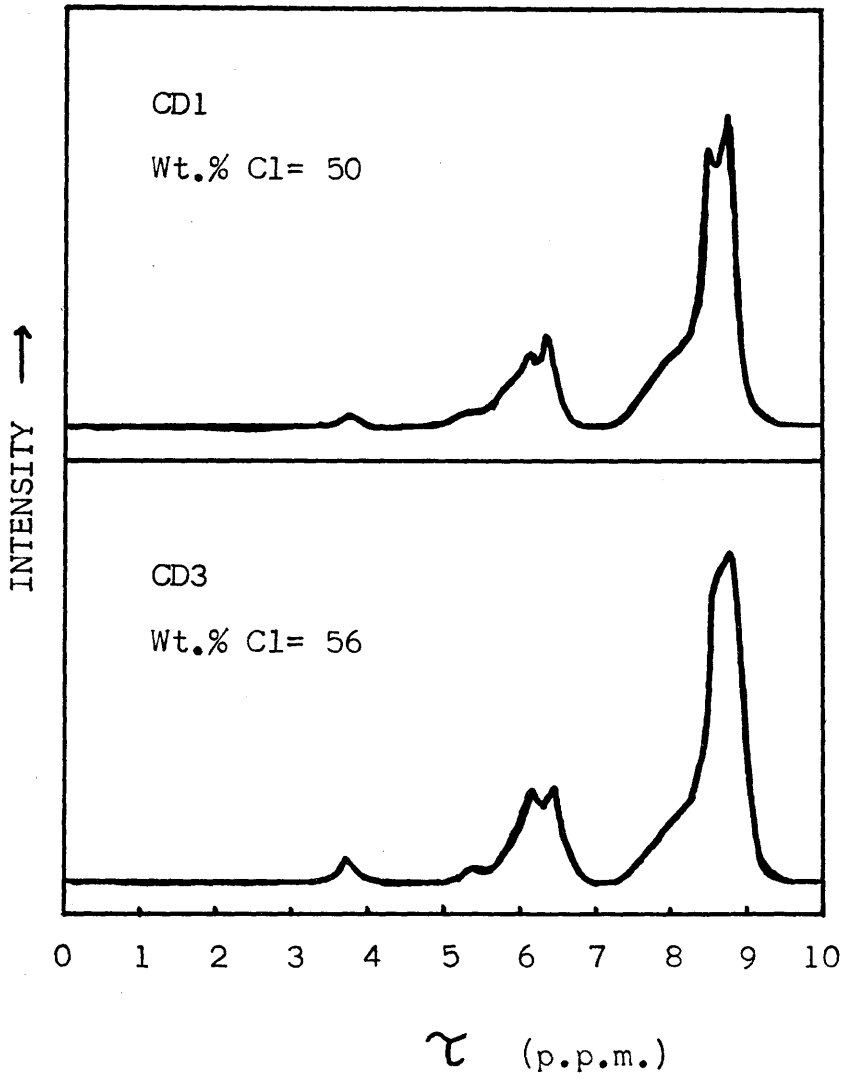


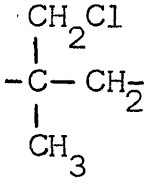
FIGURE 44. P.M.R. SPECTRA.



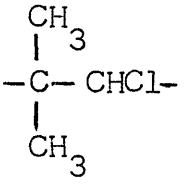
corresponding to the methylene and methyl hydrogens respectively.[94,121] Assignment of structures to new peaks in the spectra of chlorinated polymers was made by reference to published τ values[122] and previous studies of chlorinated polymers[120,123] and hydrocarbons.[124]

In polymers with less than one chlorine atom per chain unit (Cl < 40%) new peaks were observed at 6.1, 6.4, 8.2, 8.5 and 8.7 p.p.m. The peak at 6.1 p.p.m. was attributed to -CHCl- units i.e. substitution at methylene groups, and the peak at 6.4 p.p.m. to $-CH_2Cl$ groups i.e. substitution at methyl groups. The new peaks in the range 8-9 p.p.m. were due to small shifts in the methyl and methylene absorptions because of nearby chlorine atoms which decreased the shielding of the hydrogen atoms. In the spectra of polymers with more than one Cl atom per unit the bands in the 8.0 - 9.0 region tended to merge into one asymmetric peak and a new peak appeared at 3.9 p.p.m., which was attributed to the presence of $-CHCl_2$ groups. This peak was very small compared to the absorption due to singly chlorinated groups. Further information was obtained by examining the area ratio of the peaks in region 8.0 - 9.0 p.p.m., (non-chlorinated groups), to the peaks in the 6.0 - 6.4 p.p.m. region (chlorinated groups). The spectrum of CD2 is taken as a specific example.

The ratio obtained from the integrated spectrum of this polymer was approximately 8:1. Since the chlorine content of this sample was 37%, i.e. almost one chlorine atom per chain unit, two possible structures were postulated;

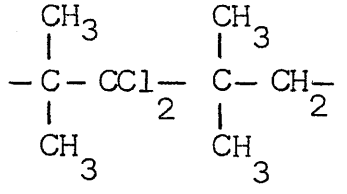


(A)



(B)

The area ratios for the spectra of A and B would be 5:2 and 6:1 respectively so that neither structure nor any combination of the structures satisfies the experimental ratio. It was inferred therefore that some units of the structure,



(C)

were present. The combination of a dichlorinated unit and an unchlorinated unit (not necessarily adjacent) would give an average of 1 Cl atom per unit and an area ratio of 14:0. A structure consisting of equal parts A,B and C would give a ratio 25:3 which is in close agreement with the

experimental ratio. Similar conclusions were drawn from the integrated spectra of the other chlorinated polymers. In all cases the presence of $-CCl_2-$ units was inferred in order to equate predicted ratios to the observed ratios. It was concluded therefore that although chlorination occurred at both the methyl and methylene groups, the substitution was not random and took place preferentially at the methylene group.

TEMPERATURE PROGRAMMED DEGRADATION.

A preliminary, qualitative picture of the effect of chlorination on the degradation properties of the polymer was obtained by studying the temperature-programmed degradation traces (Chapter 2, section 3(iv)). The marked decrease in the thermal stability of the chlorinated derivatives is illustrated in figures 45 - 48. The actual temperatures of degradation used in these figures were derived from the oven temperatures using figure 12.

The following observations and conclusions were made from these experimental curves.

(a) Small peaks which appeared below 150^{o}C were attributed to the evolution of solvent and volatile impurities.

FIGURE 45. TEMPERATURE PROGRAMMED DEGRADATION OF POLYISOBUTENE AND END-GROUP CHLORINATED POLYISOBUTENE.

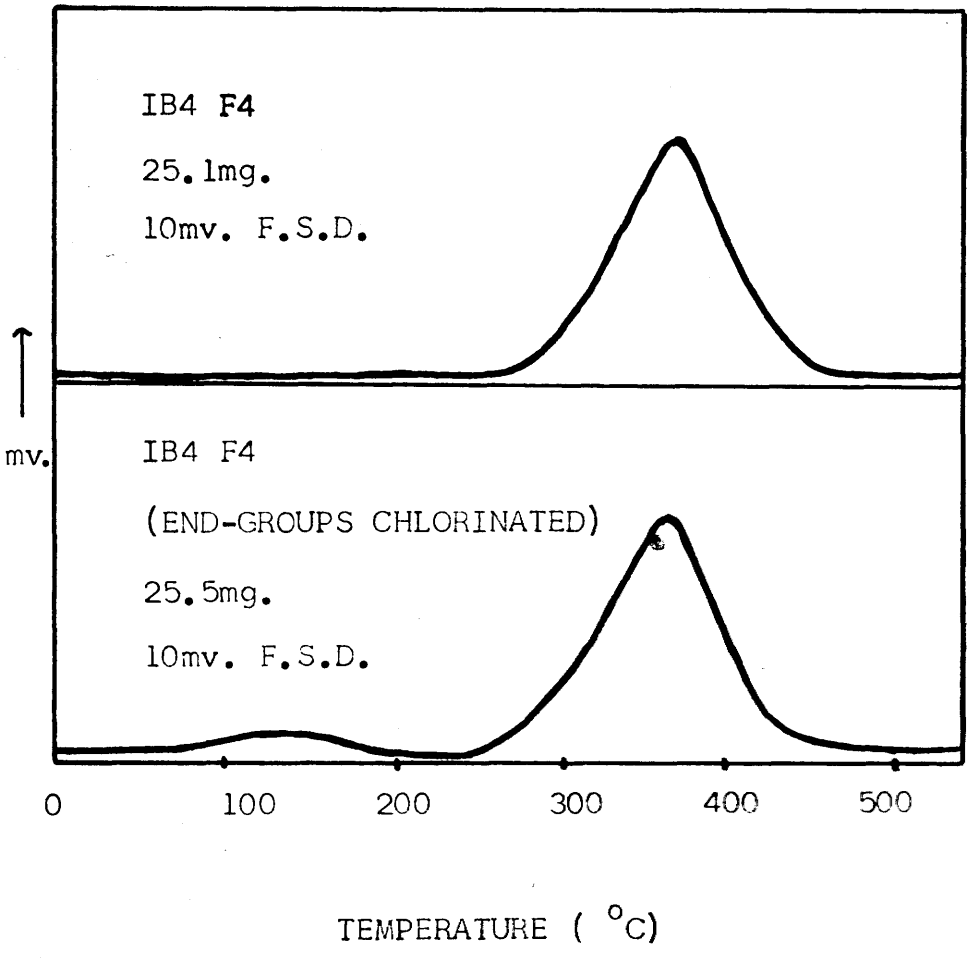


FIGURE 46. TEMPERATURE PROGRAMMED DEGRADATION OF CHLORINATED POLYMERS.

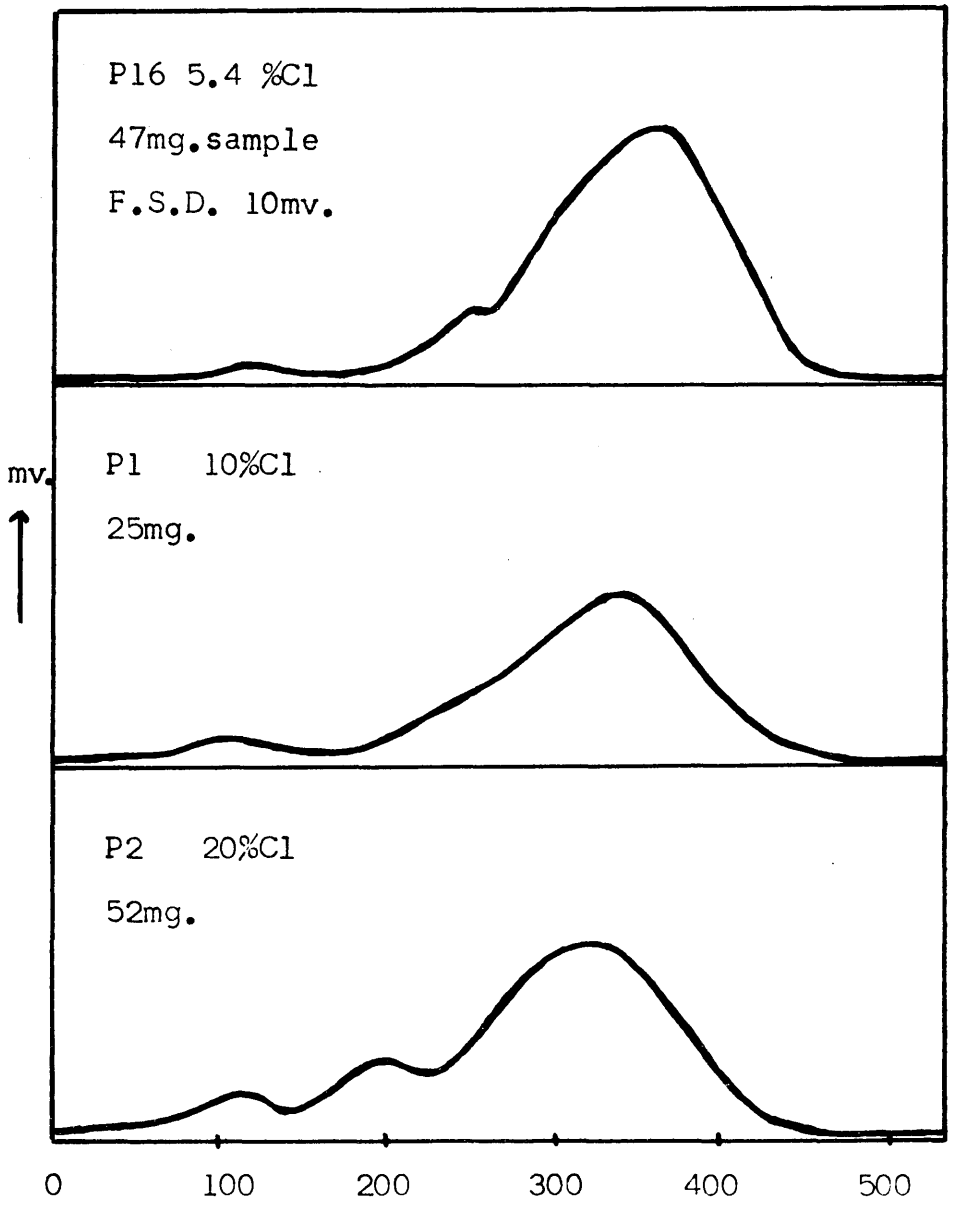


FIGURE 47. TEMPERATURE PROGRAMMED DEGRADATION OF CHLORINATED POLYMERS.

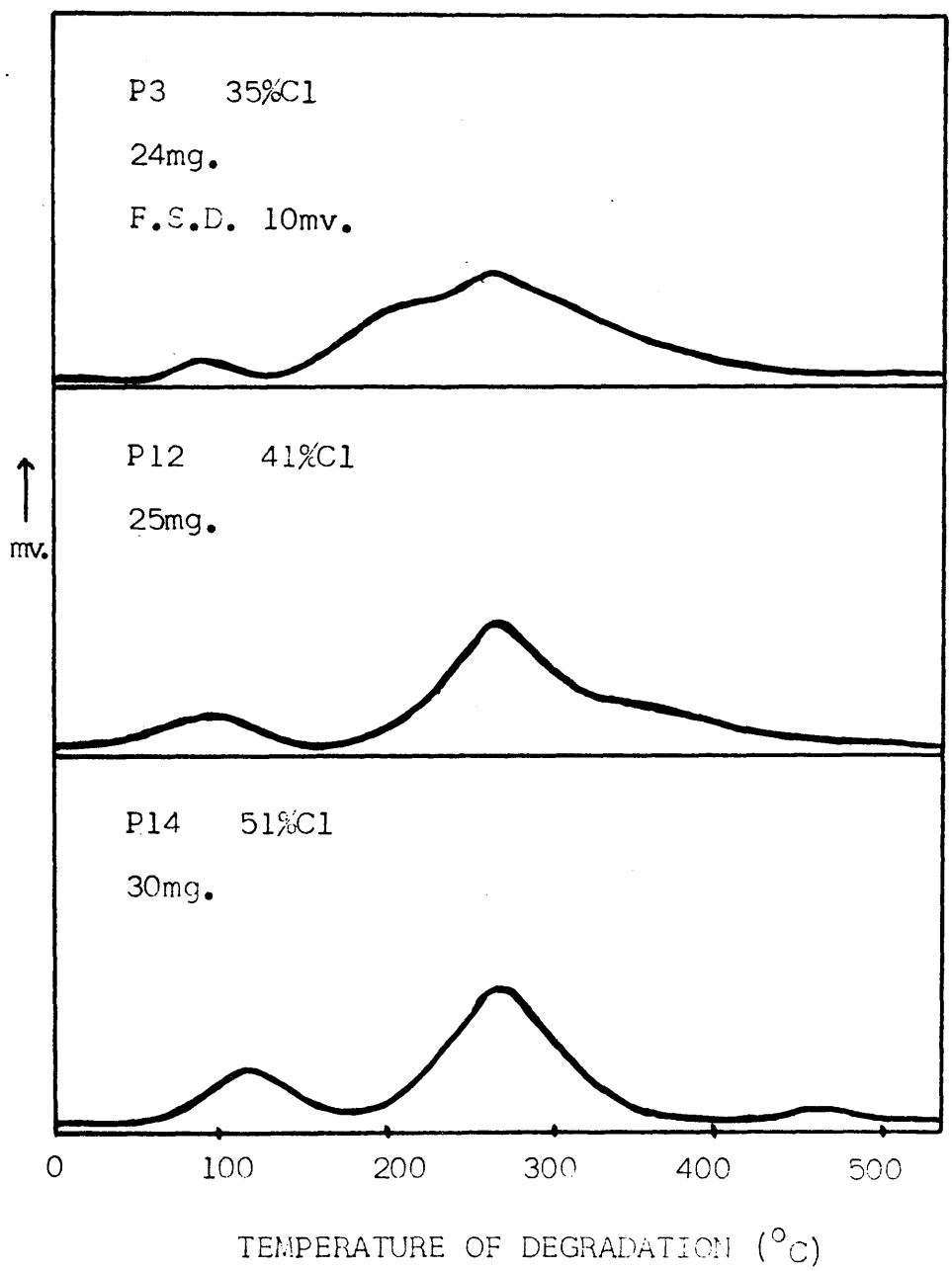
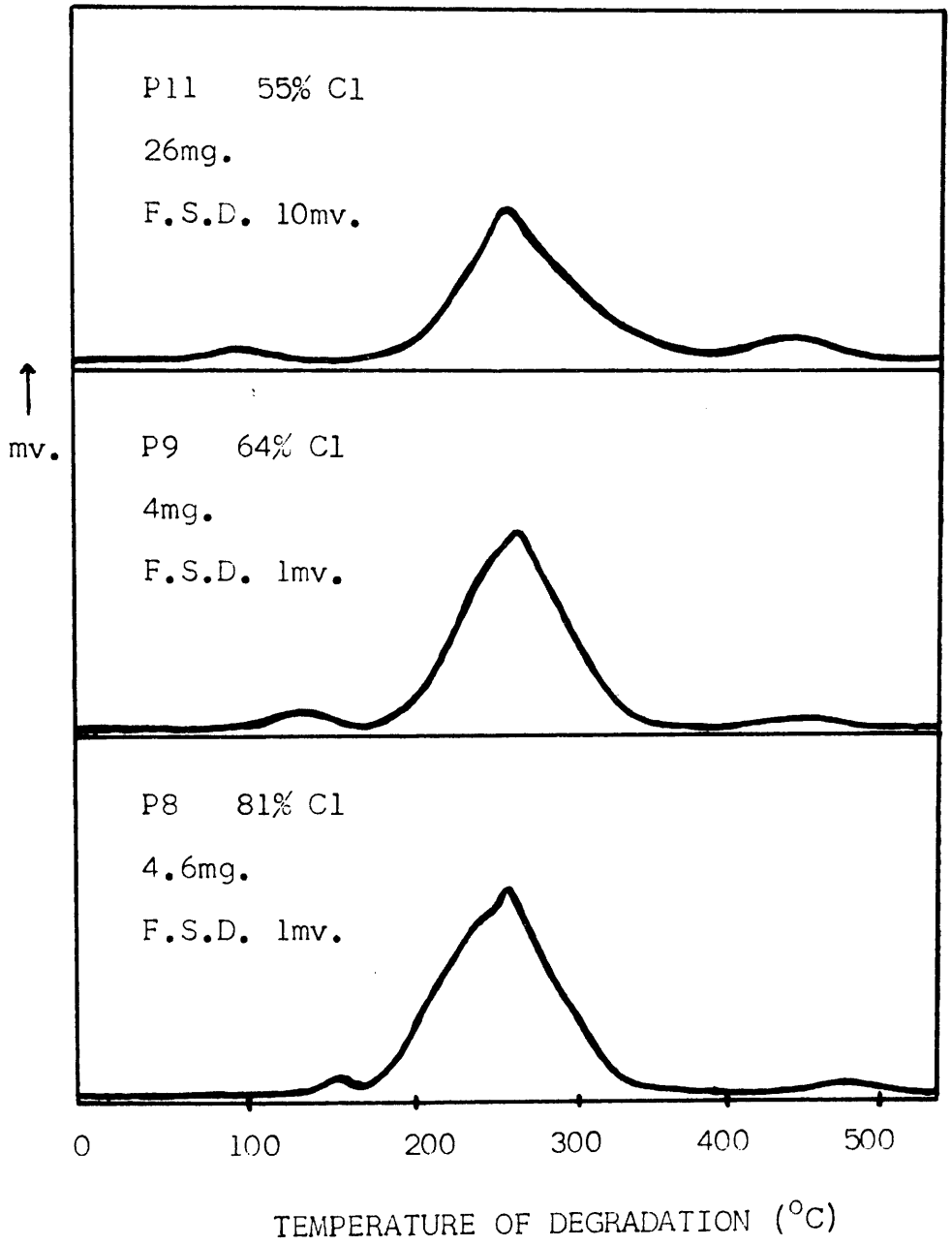


FIGURE 48. TEMPERATURE PROGRAMMED DEGRADATION OF CHLORINATED POLYMERS.



(b) Chlorine content less than 20%.

The peak observed for polyisobutene broadened out as the degree of chlorination increased since degradation commenced at a lower temperature; the shift in starting temperature was approximately 100°, giving a temperature in the region 170 - 180°C. The low-temperature degradation resulted in a shoulder or small peak on the main peak. On completion of these degradations there was no residue in the tube but a colourless cold-ring fraction was formed.

(c) Chlorine content: 20 - 45%.

The curves obtained for polymers in this range were spread out over a wide temperature range and appeared to envelop both the low-temperature degradation characteristic of the chlorinated products and the degradation at higher temperatures which was observed for the parent polyisobutene. Because of the higher contribution of low-temperature degradation, the peak maximum now appeared at lower temperatures (approximately, 270°C). Polymers in this group showed the greatest thermal instability, degradation starting at temperatures around 150°C. The polymers degraded completely to cold-ring fraction, which was pale-yellow, and volatiles which had a pungent odour.

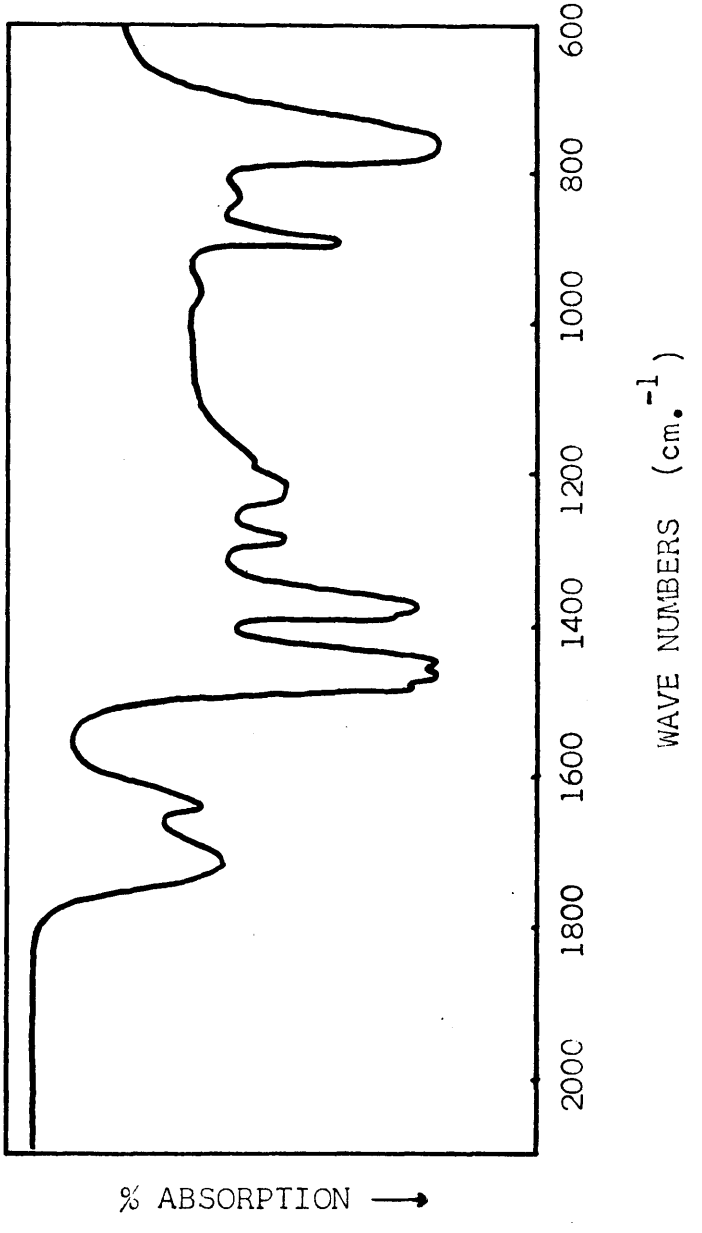
(d) Chlorine content greater than 45%.

Little variation could be observed in the degradation features exhibited in this group. The main peak was sharper corresponding to a more uniform degradation mechanism but the initiation temperature was a little higher than for the polymers of the previous group. The appearance of a new, shallow peak at high temperatures distinguished this group from less highly chlorinated polymers. Examination of the degradation tube after degradation revealed not only a yellow cold-ring fraction but also a black residue which was insoluble in carbon tetrachloride or chloroform. It was concluded that in this group the primary evolution of volatiles corresponding to the main peak resulted in a residue which degraded further at higher temperatures to produce a small quantity of volatile product and a black residue.

Nature of Products.

Since the temperature-programmed degradations represented but a preliminary investigation into the degradation behaviour of these polymers, detailed study of the products was not attempted at this stage. It was noted, however, that the volatiles obtained from polymers of low chlorine content had a hydrocarbon odour reminiscent of isobutene. The volatiles obtained from polymers of

FIGURE 49. I.R. SPECTRUM OF A YELLOW COLD-RING FRACTION.



chlorine content > 20% had a distinctive pungent odour and produced an acid reaction when dissolved in water. It was deduced therefore that hydrogen chloride might be present in the volatile products from chlorinated polymers.

The I.R. spectrum of a yellow cold fraction (in the form of a thin film between two salt plates) is shown in figure 49. This can be compared to that of the parent, P13, which is shown in figure 42. From the new peaks at 890, 1640 and 1710cm^{-1} it was deduced that double bonds of the exomethylene type and carbonyl structures were present in the cold-ring fraction. The C-Cl absorptions at 760 and 1290cm^{-1} were again significant so that some chlorine was still present in the cold-ring product.

CHAPTER 6.

ISOTHERMAL DEGRADATION OF CHLORINATED POLYISOBUTENE.

INTRODUCTION.

The kinetics of the degradation of chlorinated polymers were studied by measuring the evolution of radioactive volatile products. The apparatus used for this purpose has been described in Chapter 2, page 70. This method of analysis yielded equivalent data to that derived from the manometric pressure gauge used in Chapter 4.for the study of the degradation of non-radioactive polymers, i.e., the count-rate of the volatiles was proportional to the pressure of the volatiles. It was also found that the build-up of radioactive products was proportional to the extent of degradation as measured by weight-loss (cf. page 129).

Details of the preparation and structure of the polymers, CD1 - CD4, used for this study have been given in Chapter 5. From the specific activity, SA(G), of the chlorine supply used to prepare each polymer, the specific activity, SA', was derived (page 68), which allowed count-rates of volatile products in the degradation apparatus to be converted into weights of chlorine (mg.Cl') in the products; the chlorine would be expected to be combined rather than elementary.

In order to relate degradations involving different starting weights of polymer and to compare the behaviours of the four polymers, the weight of chlorine in the products was expressed as a percentage of the amount of chlorine originally present in the sample, Cl'/Cl_o . The amount of evolved chlorine could alternatively be expressed as a function of the weight of the sample, Cl'/W_o . The two methods of presenting the observed data are basically equivalent since the two functions are proportional to each other. Kinetic studies of the polymers were supplemented by analytical investigations of the products of degradation and by the study of molecular weight changes.

DEGRADATION OF CHLORINATED POLYMERS.

Degradation was studied in the temperature range, 190 - 240°C. The sample size was usually about 40 - 50mg., but in some experiments larger samples were used in order to perform further studies, e.g., M.W. analysis, on the residues of degradation. The results obtained are presented in tables 30 - 33 and shown graphically in figures 50 - 53. It was observed from these results that the evolution of radioactive products was initially rapid, but tended to level off as the degradation proceeded. This effect was especially marked for polymers CD2 and CD4 which had lower chlorine contents than polymers CD1 and CD3.

TABLE 30. DEGRADATION OF POLYMER CD1; Wt.% Cl = 50.2,

1.5 ATOMS Cl PER MONOMER UNIT.

	Time of degradation	Count-rate in volatiles	Wt.Cl'	Cl'/Cl_o
	min.	cpm.	mg.	%
W_o = 40.0mg.	15	58.1	0.59	2.96
	32	91.0	0.93	4.65
T = 200°C.	60	145	1.48	7.40
	90	191	1.95	9.75
*SA' = 97.8cpm/mg.Cl	120	223	2.28	11.4
	180	286	2.92	14.6
	240	345	3.52	17.6
	300	384	3.92	19.6
	>1000	1086	11.10	55.5
W_o = 41.0mg.	30	118	1.67	8.15
	90	245	3.49	17.0
T = 210°C.	180	353	5.03	24.5
	295	444	6.30	30.7
SA' = 70.2cpm/mg.Cl	>1000	795	11.33	55.2
W_o = 40.0mg.	10	219	1.40	7.0
	30	446	2.84	14.2
T = 220°C.	60	656	4.18	20.9
	100	857	5.46	27.3
SA' = 157cpm/mg.Cl	200	1050	7.32	36.6
	300	1288	8.20	41.0
W_o = 40.6mg.	30	451	4.60	22.6
	60	625	6.37	31.4
T = 230°C.	90	730	7.45	36.7
	150	868	8.85	43.6
SA' = 97.8cpm/mg.Cl	200	938	9.57	47.1
	270	979	10.00	49.2
	>1000	1133	11.56	57.0

* Different values of SA' arise from use of different counting assemblies.

TABLE 31. DEGRADATION OF POLYMER CD2; Wt.% Cl = 37.0,

1.0 ATOMS Cl PER MONOMER UNIT.

SA' = 121 cpm/mg.Cl.

	Time of degradation	Count-rate in volatiles	Wt.Cl'	Cl'/Cl_o
	min.	cpm.	mg.	%
T=200°C. W_o=59.0mg.	10	143	1.18	5.4
68.2	33	263	2.17	8.6
81.2	60	435	3.60	12.0
83.0	120	569	4.70	15.3
85.6	240	792	6.55	20.6
T = 210°C.	10	211	1.75	11.5
	30	359	2.97	19.5
W_o = 41.0mg.	60	445	3.68	24.2
	100	501	4.15	27.3
	200	615	5.08	33.4
	300	691	5.71	37.6
	360	700	5.78	38.0
T = 220°C.	10	366	3.02	19.6
	30	463	3.83	24.6
W_o = 42.0mg.	60	556	4.60	29.6
	120	652	5.40	34.7
	180	708	5.85	37.7
	240	730	6.03	38.8
	300	748	6.18	39.7
	400	772	6.39	41.1
	>1000	915	7.55	48.5
T = 230°C.	15	418	3.46	22.7
	30	495	4.10	27.0
W_o = 41.0mg.	60	581	4.80	31.6
	120	656	5.43	35.7
	180	711	5.87	38.6
	240	736	6.10	40.1
	300	761	6.29	41.3
	400	771	6.37	41.9
T = 240°C.	11	509	4.21	28.3
	30	642	5.30	35.6
W_o = 40.2mg.	60	717	5.93	39.8
	120	763	6.30	42.2
	200	790	6.53	43.8
	300	812	6.71	45.0
	400	823	6.80	45.6

TABLE 32. DEGRADATION OF POLYMER CD3; Wt.% Cl = 56.0,

2 Cl ATOMS PER MONOMER UNIT.

SA' = 352 cpm./mg.Cl.

	Time of degradation min.	Count-rate in volatiles cpm.	Wt.Cl' mg.	Cl'/Cl_o %
T=200°C. W_o=68.2mg.	10	219	0.62	1.63
70.6	30	466	1.33	3.36
70.0	60	753	2.14	5.47
71.0	120	1240	3.53	8.85
76.6	240	2004	5.68	13.30
T=210°C. W_o=40.2mg.	10	194	0.55	2.45
	30	456	1.30	5.75
	60	763	2.15	9.62
	120	1190	3.33	15.0
	180	1478	4.20	18.7
	240	1698	4.82	21.4
	300	1926	5.47	24.4
T=220°C. W_o=41.2mg.	10	471	1.34	5.8
	30	909	2.54	11.2
	60	1356	3.85	16.7
	120	1931	5.48	23.8
	180	2304	6.55	28.4
	240	2623	7.47	32.4
	300	2838	7.84	34.0
T=230°C. W_o=40.0mg.	10	874	2.48	11.1
	30	1520	4.32	19.2
	60	2090	5.94	26.5
	120	2690	7.64	34.1
	200	3128	8.90	39.7
	300	3389	9.63	43.0
T=240°C. W_o=40.0mg.	10	1329	3.78	16.9
	30	2202	6.26	27.9
	60	2777	7.88	35.2
	120	3332	9.46	42.2
	200	3567	10.13	45.3
	300	3755	10.67	47.6

TABLE 33. DEGRADATION OF POLYMER CD4; Wt.% Cl = 28.4,
0.5 Cl ATOMS PER MONOMER UNIT.
SA' = 812 cpm./mg.Cl.

	Time of degradation min.	Count-rate in volatiles cpm.	Wt.Cl' mg.	Cl'/Cl_o %
T=190°C. W_o=51.5mg.	10	358	0.44	3.7
	30	567	0.70	5.8
	60	796	0.98	8.1
	120	1062	1.31	11.1
	240	1340	1.65	14.0
T=200°C. W_o=52.0mg.	10	495	0.61	5.0
63.0	30	1126	1.39	9.4
65.0	60	1688	2.08	13.7
67.3	120	1912	2.36	15.0
70.5	240	2504	3.08	18.7
T=210°C. W_o=50.2mg.	10	762	0.94	8.0
	30	1240	1.53	13.0
	60	1567	1.93	16.4
	120	1890	2.33	19.8
	240	2326	2.87	24.4
T=220°C. W_o=50.2mg.	10	1166	1.44	12.2
	30	1735	2.14	18.2
	60	2114	2.60	22.1
	120	2539	3.12	26.6
	240	3021	3.72	31.6

FIGURE 50. DEGRADATION CURVES FOR POLYMER CD1.

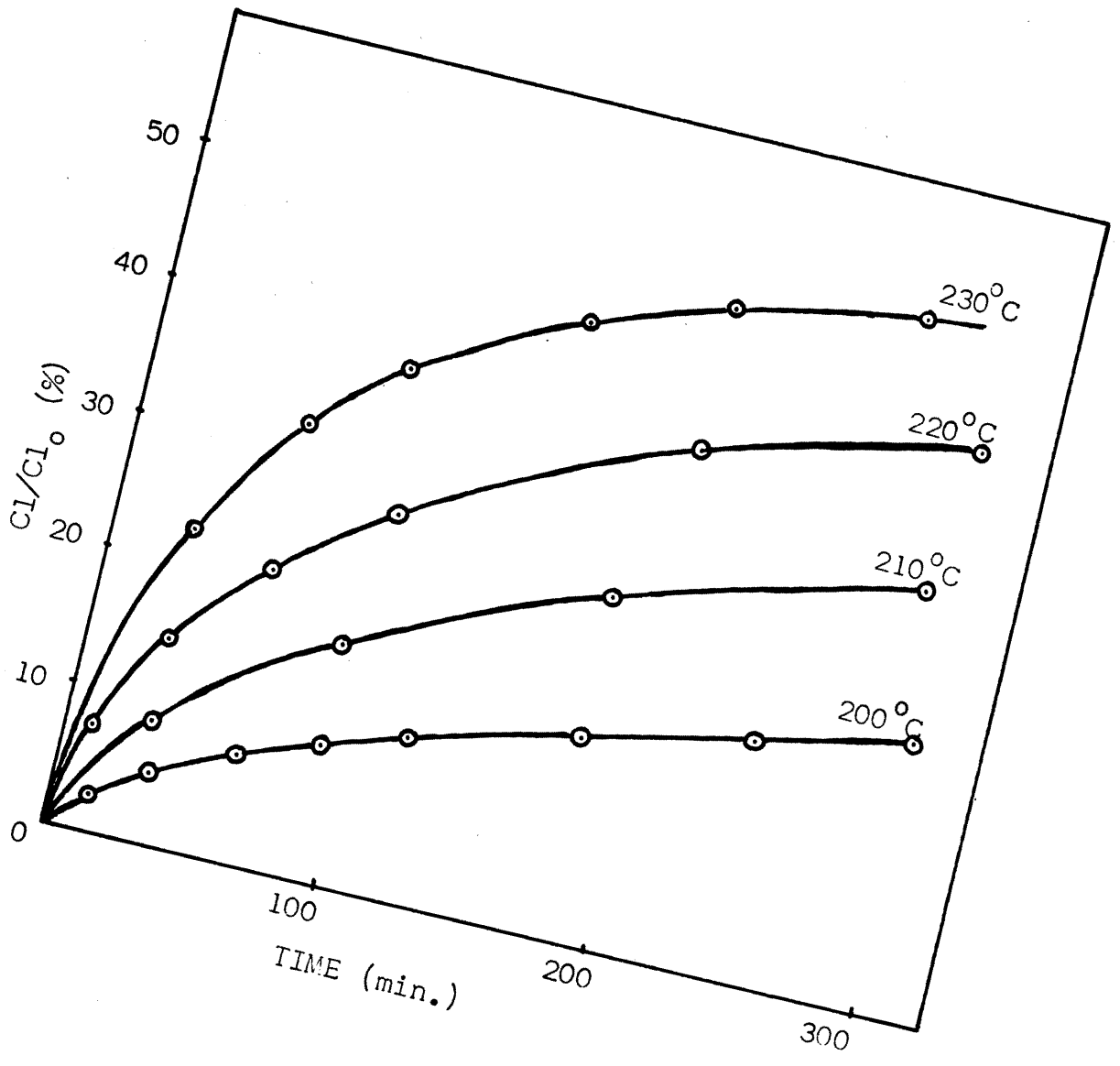


FIGURE 51. DEGRADATION CURVES FOR POLYMER CD2.

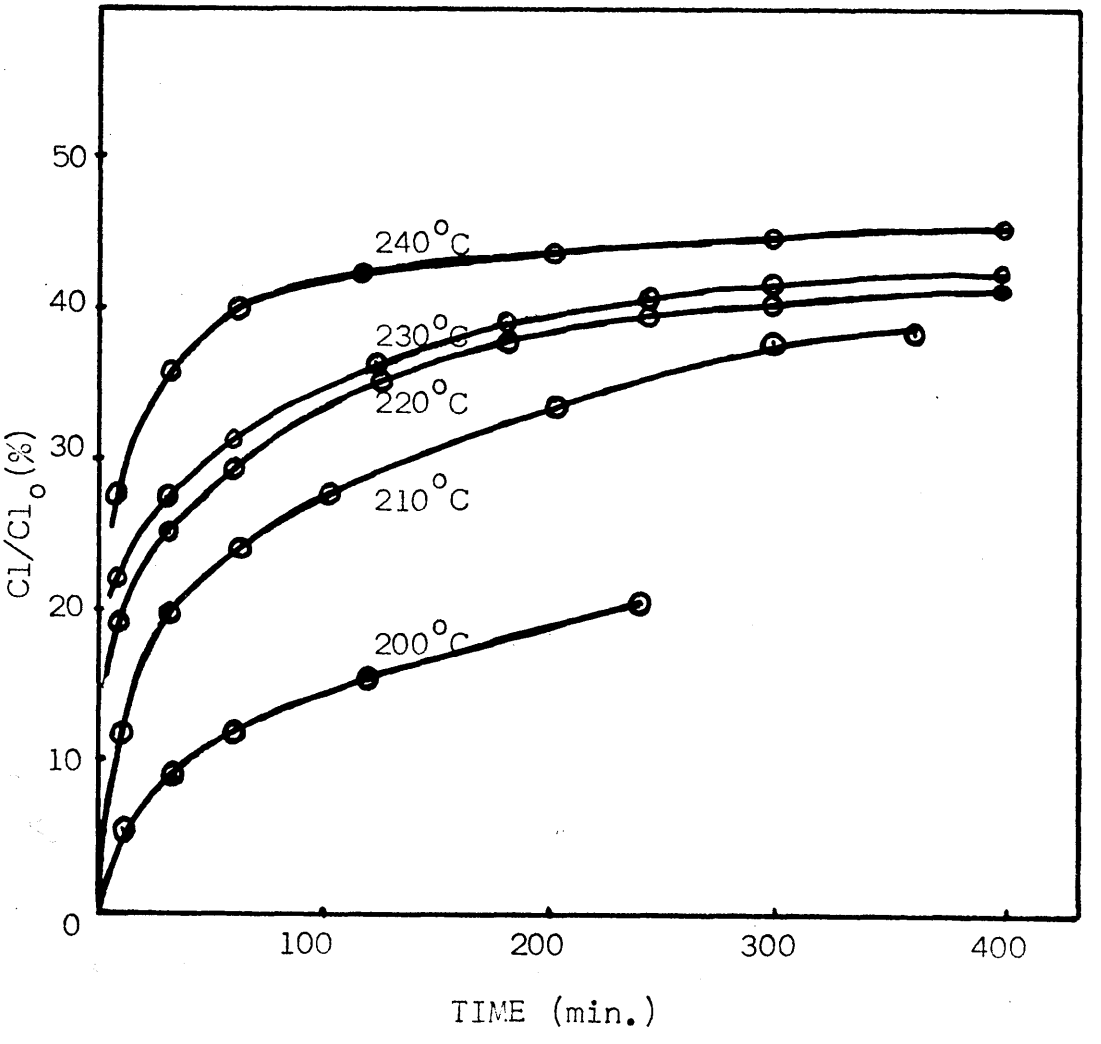


FIGURE 52. DEGRADATION CURVES FOR POLYMER CD3.

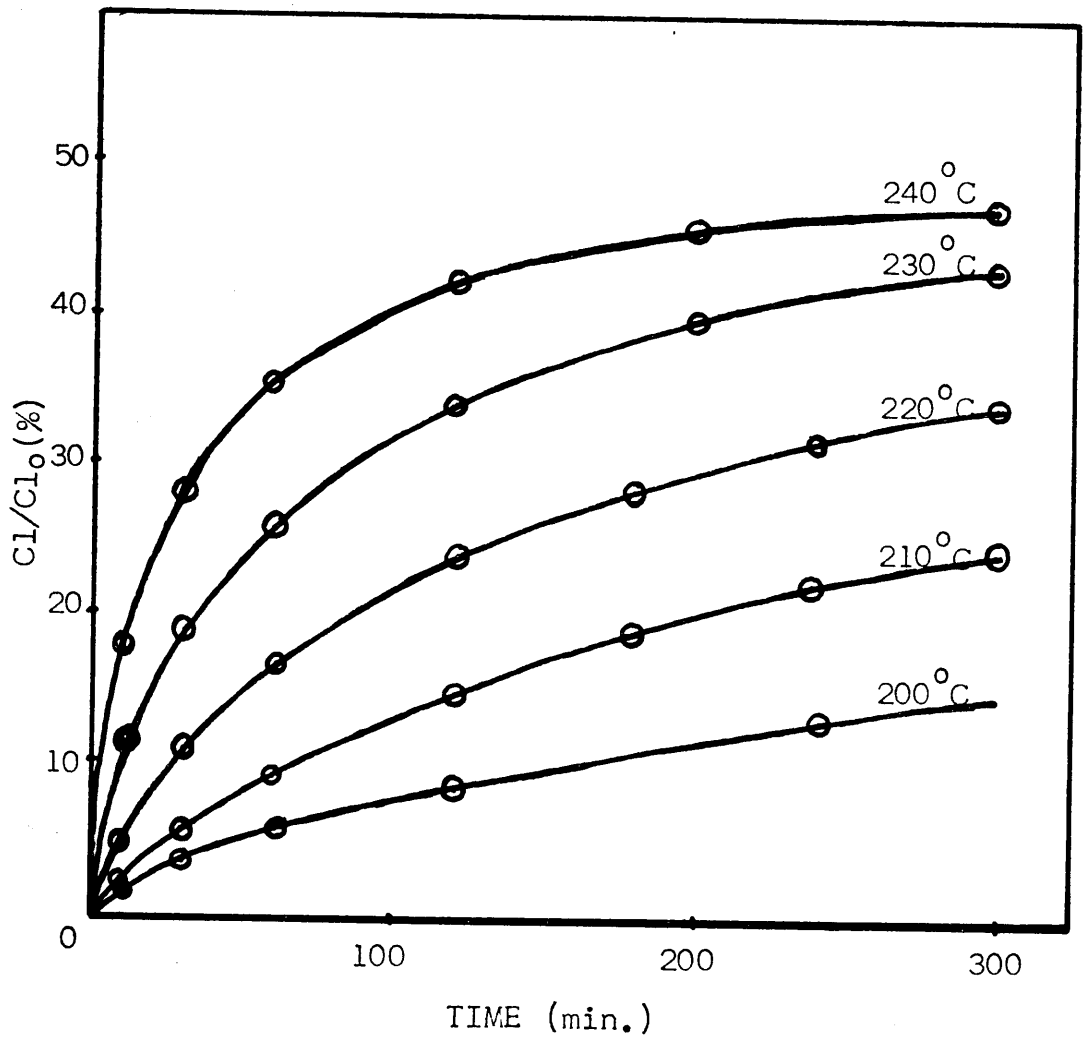
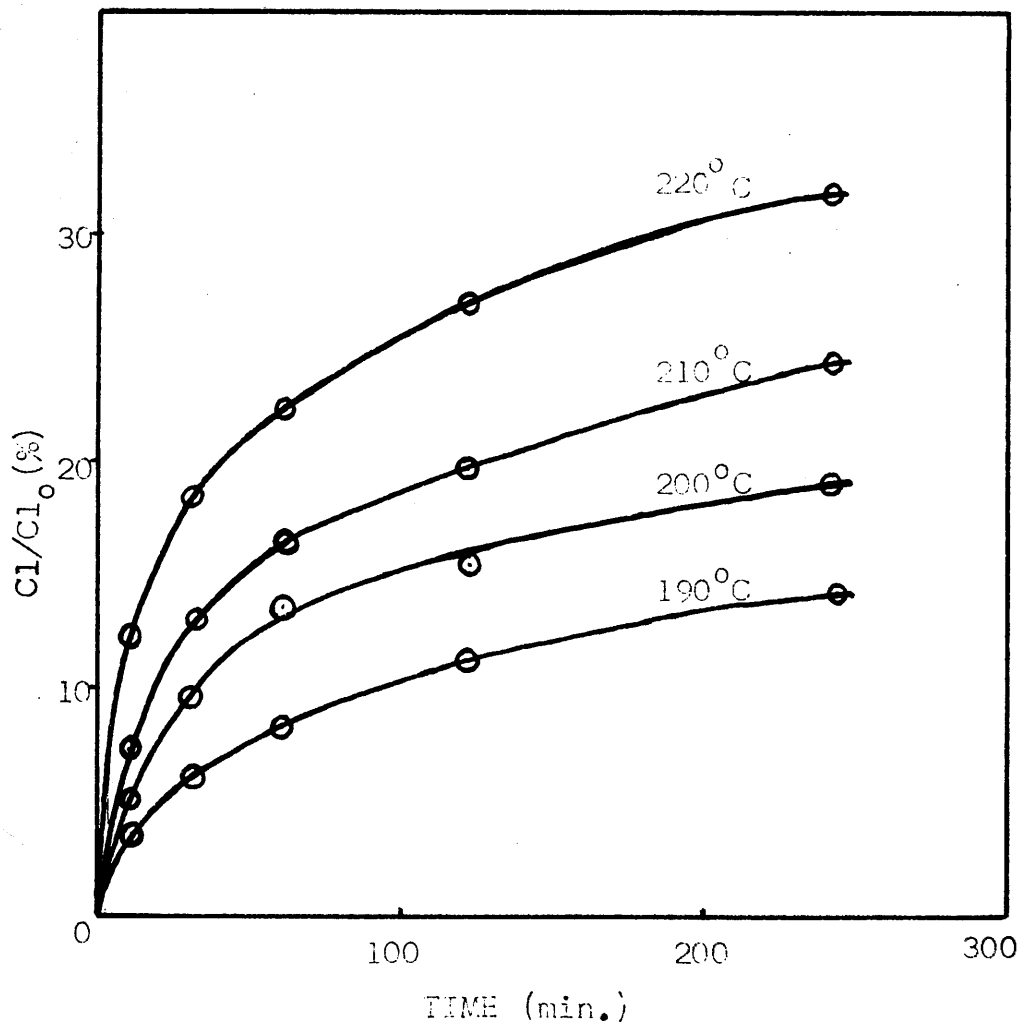


FIGURE 53. DEGRADATION CURVES FOR POLYMER CD4.



The rapid fall in the rate of degradation with respect to time and extent of degradation (Cl'/Cl_o) was reflected in the pirani readings taken during each experiment. Figures 54 and 55 show the pirani readings as a function of Cl'/Cl_o for polymers CD1 and CD4, which represent high and low chlorine contents, respectively. The calculation of rates from Cl'/Cl_o - time data (cf. page 131) yields equivalent information to that derived from pirani measurements.

A number of degradation experiments were continued for periods of up to 24 hours in order to observe the effect of prolonged degradation; some of these are included in tables 30 and 31. As is reflected in figure 51, for example, the polymers tended to become stable at the temperatures of degradation used and the value of Cl'/Cl_o did not approach 100%. The actual values of Cl'/Cl_o (24hrs.) showed some variation for different polymers e.g. 55-57% for polymer CD1 and 47-50% for polymer CD2, but were fairly constant for each polymer over the range of temperatures studied. Thus, degradation had virtually ceased after prolonged heating in the range 200-240°C, but further decomposition of the resulting residue could be induced at temperatures above 250°C. It was observed that the degradation residues, which were yellow in colour, tended to become insoluble in chloroform after prolonged heating; the effect was most marked for polymers CD1 and CD3. The residue of polymer CD4 remained soluble even at high extents of degradation.

FIGURE 54. RATE CURVES FOR POLYMER CD1.

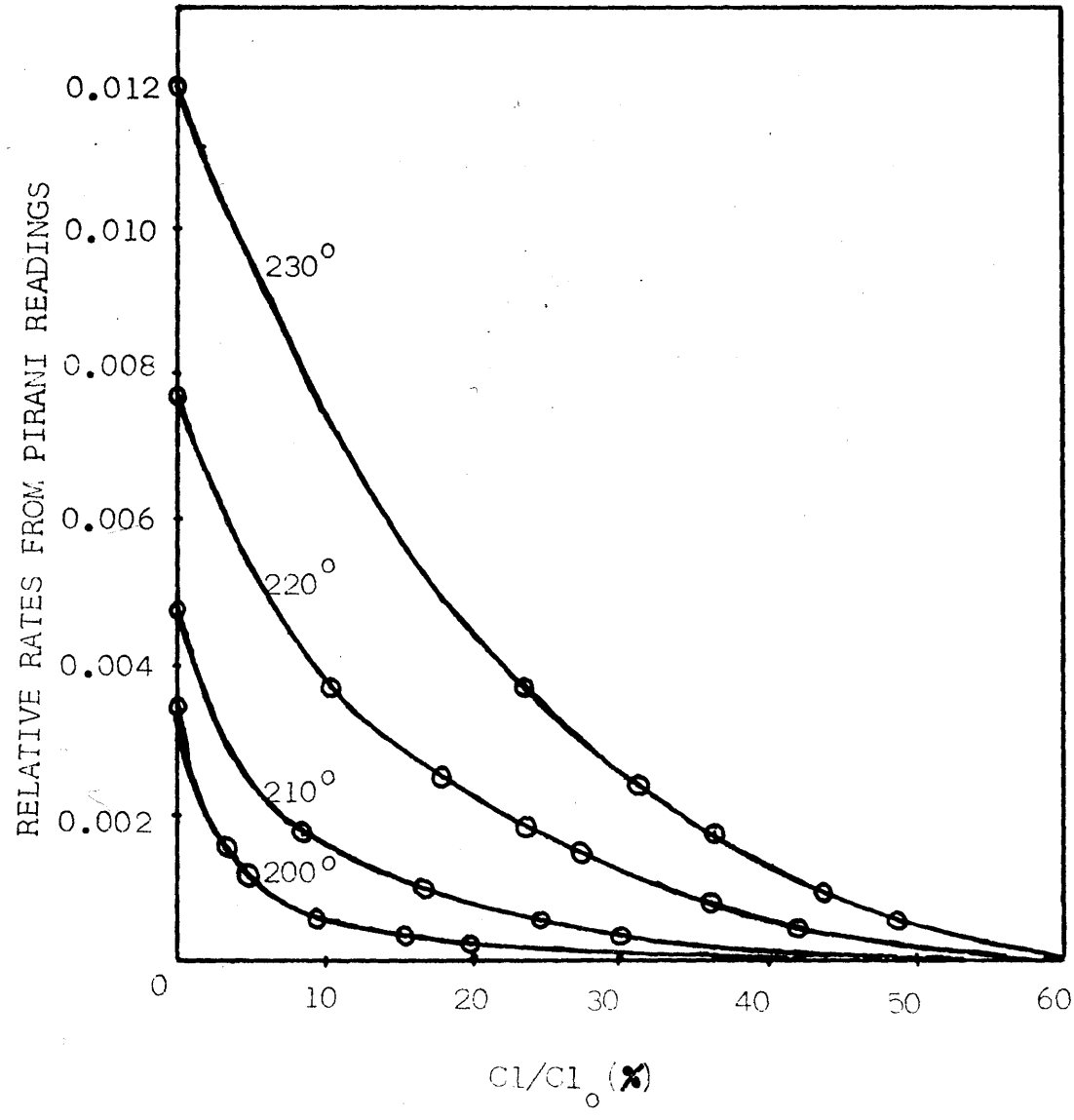
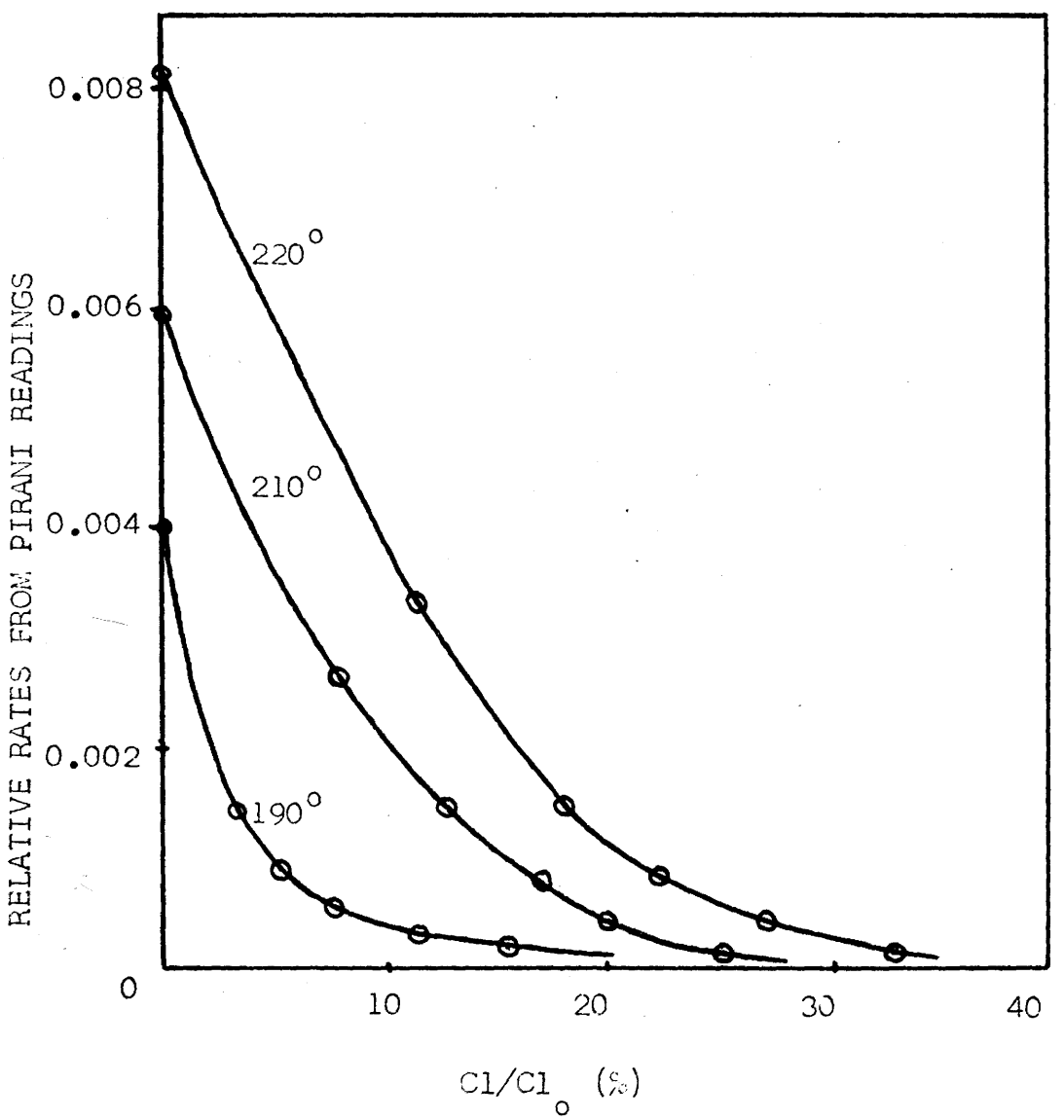


FIGURE 55. RATE CURVES FOR POLYMER CD4.



MOLECULAR WEIGHT CHANGES DURING DEGRADATION.

The residues at various times of degradation at 200°C were dissolved in chloroform and the molecular weights measured using the High-Speed osmometer. It was found that almost every sample tended to diffuse in the osmometer so that the data given in table 34 represent approximate values of the molecular weight. Qualitative conclusions can, however, be drawn from these results. With the exception of the scattered results obtained for polymer CD2, the molecular weights showed a similar trend. During the initial stages of degradation, the molecular weights decreased to approximately 10,000. This is clearly seen for polymer CD4, the initial molecular weight of which was higher than the others. After approximately 30 minutes degradation, little further change could be detected in the molecular weights. Since the molecular weights remained low, it was concluded that cross-linking reactions, which would have explained the development of insolubility in some degraded polymers, were not predominant at any stage of the degradation.

The initial fall in molecular weight suggests that some scissions occurred, but owing to the relatively low starting molecular weights, a proper insight into the chain-breaking mechanism could not be obtained (cf. Chapter 4).

PRODUCT ANALYSIS.

The degradation products of the chlorinated polyisobutenes consisted of a volatile fraction which was collected in the cooled trap (Fig.8) and an involatile fraction which remained in the degradation tube, partly as a residue in the bottom of the tube and partly as a film on the walls of the tube. Since there was no increase in pressure when degradation was changed from an open system to a closed one, it was concluded that all the volatile degradation products were condensable.

Volatile Fraction.

In many degradation experiments, the products were ultimately condensed into water and the resulting solution titrated against standard NaOH solution (page 71). As a result of the titres obtained, it was concluded that HCl was the major constituent of the volatile products. The amount of chlorine consisting of HCl, Cl'(HCl), was compared to the total amount of chlorine in the products, Cl'. The results of some fifty experiments indicated that Cl'(HCl)/Cl' was 80 - 100%. The fluctuations in the ratio were probably caused by errors in estimating the small quantities of HCl rather than from variations in the product composition. The high proportion of HCl was apparent for all four polymers.

The distribution of the chlorine between the volatile products and the residue has been previously discussed (page 186 et seq.). The relative weights of the volatile and residue fractions depended on the extent of degradation but a limiting ratio was obtained after 24 hours heating at each temperature (table 35). Thus, the more highly chlorinated polymer gave a slightly larger volatile fraction with respect to the original weight.

TABLE 35. LIMITING WEIGHT FRACTIONS OF VOLATILE PRODUCTS.

Temperature °C	$W_{volatiles}/W_o$ (24hrs.) %	
	CD1	CD2
200	26	23
210	25	22
220	33	25
230	29	21
240	-	21

Since the volatiles usually possessed a peculiar odour which was different from that of HCl and since the weights of the volatile fractions were generally higher than would have been accounted for by the observed HCl'(Cl') values, it was concluded that small amounts of other products were also present. The design of the apparatus did not permit very accurate weight measurements to be made so that the

ratio $W_{HCl(Cl')} / W_{Volatiles}$ tended to fluctuate. In table 36 a few degradations have been selected and the weight of HCl derived from the Cl' value is compared to the observed weight of the volatile fraction. Despite the difficulty of obtaining precise information, it was evident that the total contribution of other products was small compared to that of HCl.

Attempts were made to identify the other products of degradation by mass spectrometry, G.L.C., and combined G.L.C. - mass spectrometry, (page 72). Little conclusive information was derived from the separate mass spectra and G.L.C. studies. The mass spectra showed a number of fragment peaks but few parent peaks (this is quite common in chlorinated compounds) so that positive analysis was difficult. Table 37 summarises the information derived from the mass spectra. Thus, there was evidence of hydrocarbon fragments and chlorinated compounds e.g. $CHCl_3$, CCl_4. Chloroform was used as a solvent to prepare the films for degradation so that its presence is not surprising. The apparent presence of styrene, however, was very surprising; the experimental spectra were in good agreement with standard spectra so that the assignment was justified. The peaks at 77 and 79 would be expected from the styrene fragmentation but they were found in other spectra which did not show the presence of styrene, so that

TABLE 36. WEIGHT FRACTION OF HCl IN VOLATILES.

Degradation Reference Polymer/Temperature/Time. (°C) (min.)	HCl(Cl') mg.	$W_{volatiles}$ mg.	$\frac{W_{HCl}}{W_{volatiles}}$ %
CD1/200/240	7.2	10.2	71
CD1/220/30	4.5	5.6	81
CD1/200/120	4.1	6.5	63
CD2/200/240	6.7	7.0	95
CD2/210/>1000	7.4	9.3	79
CD2/230/>1000	7.5	9.8	77
CD3/210/300	5.6	6.8	82
CD3/230/300	10.0	11.6	86
CD3/240/300	11.0	12.0	92
CD4/190/240	1.7	2.1	81

TABLE 37. SIGNIFICANT M/e SIGNALS IN MASS SPECTRA.

Polymer	M/e signal	Assignment
CD1	117, 119, 121, 123	CCl_4
	83, 85, 87	$CHCl_3$
	56	Butene (C_4)
	57	C_4H_9 fragment
	41-43	C_3 fragments
	69, 71	C_5 fragments?
CD2	Hydrocarbon fragments as in CD1 +	
	83, 85, 87	$CHCl_3$(solvent)
CD3	Hydrocarbon fragments +	
	77, 79	C_6H_5 fragment?
	104	Styrene
CD4	Hydrocarbon fragments +	
	83, 85, 87	$CHCl_3$(solvent)
	77, 79	C_6H_5 fragment
	104	Styrene

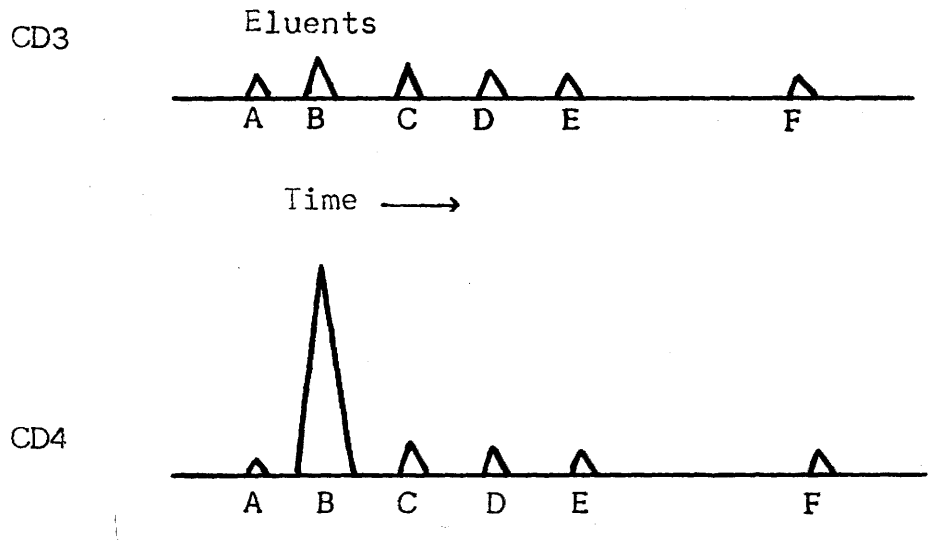
a second aromatic compound may have been present.

Samples of the degradation products of polymers CD3 and CD4, the polymers of highest and lowest Cl content, were analysed by combined G.L.C. - mass spectrometry after removal of HCl. The analysis is illustrated diagrammatically in figure 56. Similar components were found for both samples. The most significant difference was that the polymer CD4 with less chlorine gave a much greater amount of isobutene. Solvent impurities, $CHCl_3$, were detected and the interesting product E which was definitely oxygenated suggested oxygenated impurities in the polymer. Carbon tetrachloride could derive from reaction of the chloroform with chlorine radicals during degradation. The remaining products are formed by depolymerisation (isobutene, chlorinated C_4 compounds) and fragmentation (methyl chloride, vinyl chloride, propyl chloride). There was no evidence in these spectra of styrene which was found in the ordinary mass spectra.

Residue Fraction.

Polyisobutene degraded completely to volatile and cold-ring fractions on prolonged heating at 300°C (Chapter 4). In the degradation of the chlorinated polymers a residue remained after prolonged heating at 200 - 240°C, and for the highly chlorinated polymers a residue remained even at

FIGURE 56. SCHEMATIC REPRESENTATION OF G.L.C.-MASS SPECTROMETRIC ANALYSIS OF VOLATILE PRODUCTS (EXCLUDING HCl).



A- Methyl chloride + vinyl chloride.

B- Isobutene + trace chloropropane (C_3H_7Cl).

C- C_4H_5Cl } probably isomers + CCl_4 (trace in D).

D- C_4H_5Cl }

E- Oxygenated compound: C_3H_7O(m/e = 59) fragment.

F- Chloroform

high temperatures (Chapter 5). A definite division of the involatile fraction into cold-ring and true residue was difficult to make since the product extended right up the walls of the tube. The cold-ring fraction was concluded to be low M.W. residue or possibly residue of low Cl content rather than a separate entity. At 200°C, the amount of low M.W. residue was small, less than 10% total residue. At higher temperatures, 230 - 250°C, the amount of cold-ring fraction became very much larger.

An interesting feature of these degradations was that the involatile products were yellow. The intensity of the colouration depended both on the time of degradation and on the chlorine content of the starting polymer. Thus the yellow colour was more noticeable for polymers of high chlorine content for the same times of degradation. It is reasonable to conclude therefore that the colour formation results from HCl loss. The exact mechanism is obscure, however; the formation of conjugated double bonds, as in P.V.C., does not seem possible in this case unless methyl groups are split out from the chain.

The chlorine content of the polymer decreased on degradation. This was expected since the major volatile product was HCl rather than chlorinated isobutene. Chlorine contents of the residues were estimated radiochemically by

counting chloroform solutions of the residues (pages 39-40). The results of these experiments are given in table 38. The figures shown in brackets represent Cl contents calculated from the observed weight of chlorine evolved (Cl') assuming that this was entirely HCl. The agreement is quite good.

TABLE 38. Cl CONTENTS OF RESIDUES.

Duration of degradation (200°C) (min.)	Cl content of residue (Wt.% Cl)			
	CD1	CD2	CD3	CD4
0	50.2	37.0	56.0	23.4
10	51.5	37.0	55.9	22.0
30	51.0	34.3	55.1	21.2
60	50.0	35.8	54.5	20.4
120	49.2	35.5	54.0	20.0
240	45.8	30.5	52.5	19.6
	(45.7)	(31.8)	(52.5)	(19.4)

I.R. spectra were obtained for the yellow residues in order to ascertain whether any new structures had been formed. The spectrum of the cold-ring fraction derived from polymer CD1 was similar to that previously described (figure 49). The changes on degradation were a reduction of the intensity of the 760cm.$^{-1}$ band (C-Cl) and the

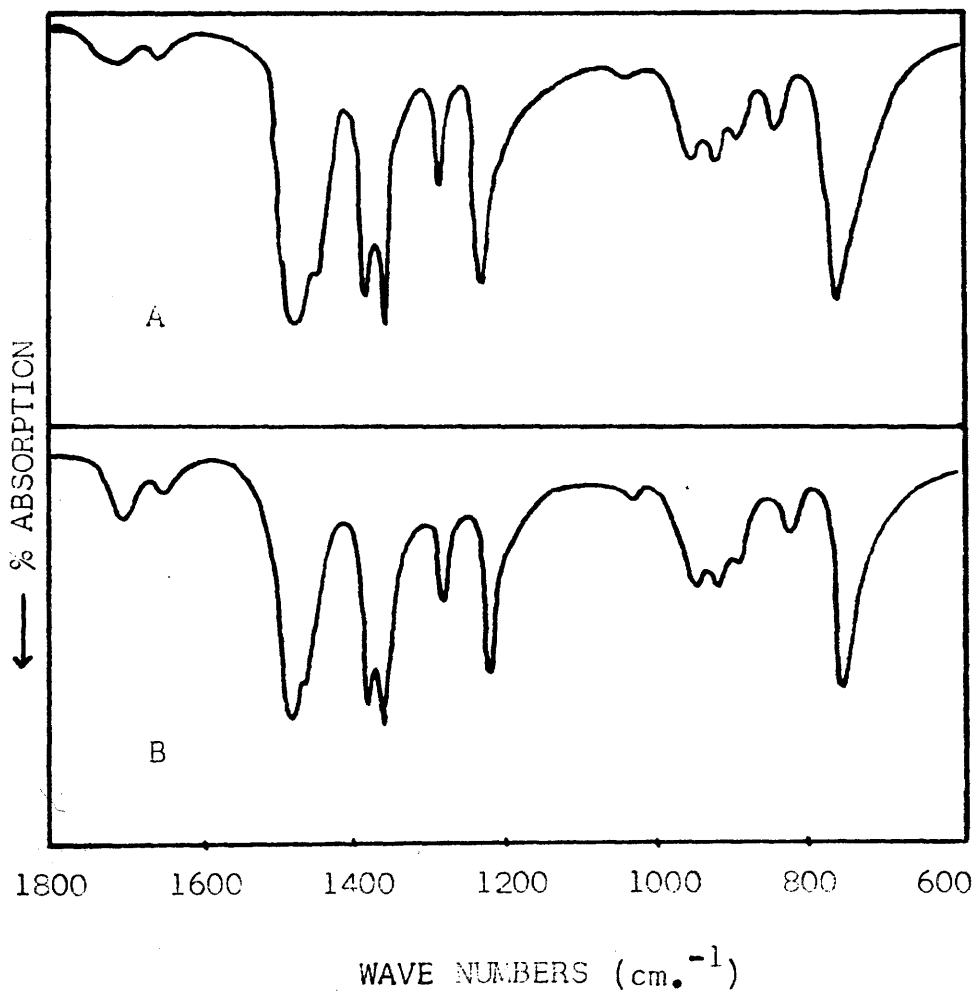
appearance of unsaturation, 890 and 1640cm^{-1}; a small hump corresponding to carbonyl absorption appeared at 1700-1720cm^{-1}. The I.R. spectra were obtained for a series of residues corresponding to the degradation of polymer CD4 at 200^{o}C for 10, 30, 60, 120 and 240 minutes. The film spectra of the residues for 10 and 240 minutes degradation are shown in figure 57. The spectra were similar to each other and to that of the cold-ring previously mentioned. The intensity of the C-Cl absorption was unchanged throughout the series, but the hump at 1700-1720cm^{-1} was more pronounced for the longer times of degradation. The double bond absorption at 890cm^{-1} remained small throughout the series.

P.M.R. spectra of corresponding series of residues from polymer CD1 and CD2 degradations were examined (cf. Chapter 5). Surprisingly, the residue spectra were identical to the parent spectra shown in figures 43 and 44. Although the chlorine content of the residue decreases with the time of degradation (table 38) no change could be detected in the relative intensities of the chlorinated peaks and the non-chlorinated peaks. The spectrum of polymer CD2 remained unchanged even after 24 hours degradation at 200^{o}C.

FIGURE 57. I.R. SPECTRA.

A - RESIDUE FROM 10 MINUTES DEGRADATION OF POLYMER CD4.

B - RESIDUE FROM 240 MINUTES DEGRADATION OF POLYMER CD4.

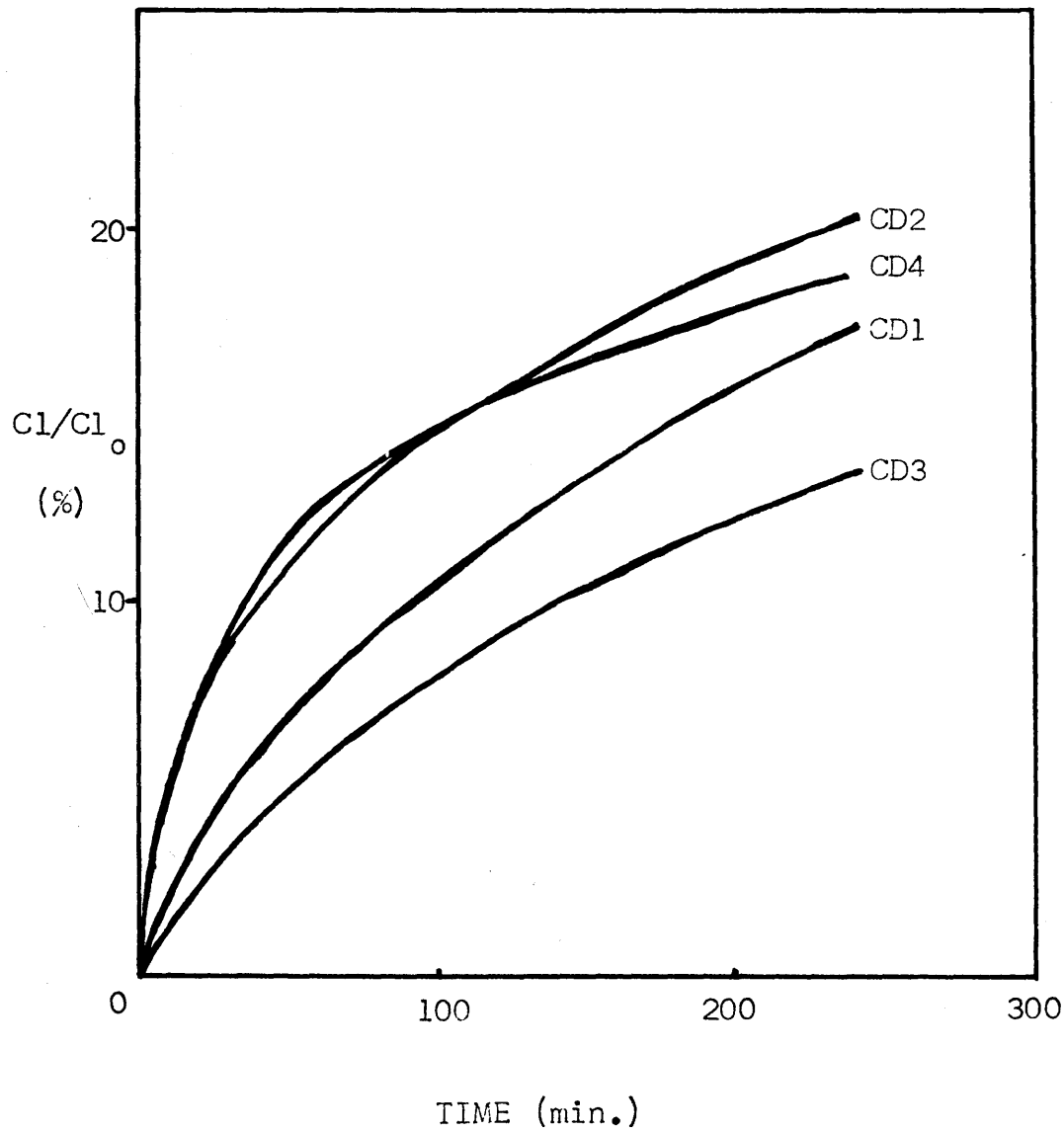


DISCUSSION.

Relative stabilities of chlorinated polymers.

In Chapter 5, the thermal stabilities of a series of chlorinated polymers were compared by inspection of temperature-programmed degradation data; it was observed that polymers of Cl content in the range 20-40% showed the lowest starting temperatures and therefore the lowest thermal stabilities. From the results of isothermal degradation experiments (tables 30-33) it is possible to make a more detailed examination of the stabilities. In figure 58, the degradations of polymers CD1-CD4 at 200°C are compared, showing the evolution of chlorine, as a percentage of the total chlorine available in the polymer, as a function of time. The initial rates of degradation(Cl'/Cl_o/min.) for polymers CD2 and CD4 were almost identical and were considerably greater than those of the other two polymers. The rate for CD1 was a little higher than that for CD3. Thus, the polymer with the highest chlorine content showed the lowest initial rate of degradation. It can be seen, however, that this picture changes as the degradations proceed. The curve for CD4 cuts the curve for CD2 after 120 minutes and would cross the CD1 curve after approximately 300 minutes. From the values of Cl'/Cl_o(24hrs.),(page 195), it is apparent that after prolonged heating the extents of

FIGURE 58. DEGRADATION OF CHLORINATED POLYMERS AT 200°C.



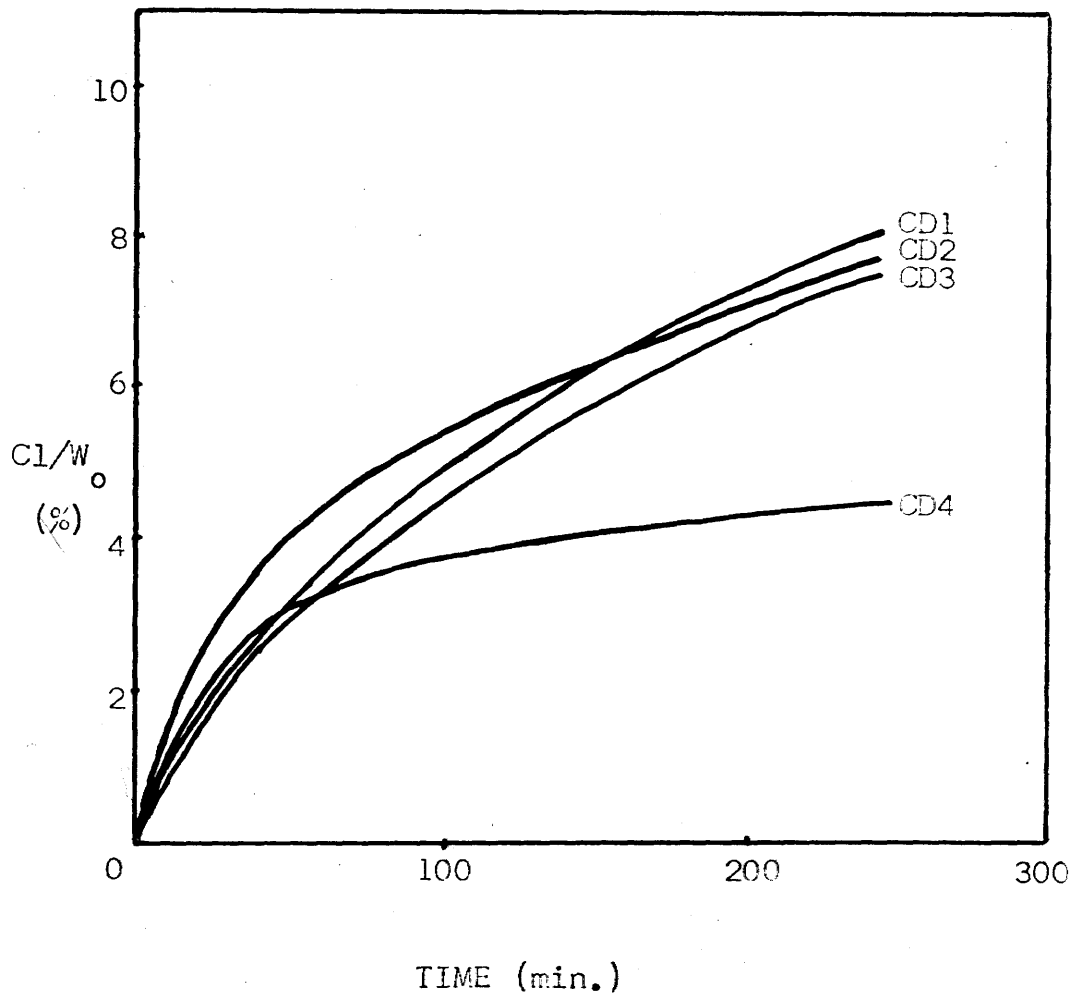
degradation in terms of Cl'/Cl_o are in the order, CD4 < CD2 < CD1 < CD3, i.e., the value of Cl'/Cl_o at infinity increases with increasing chlorine content of the polymer.

The degradations of the four polymers were also compared by expressing the amount of chlorine evolved as a percentage of the total weight of sample. The values of this function are easily derived from the Cl'/Cl_o data and are presented in table 39. The curves obtained by plotting Cl'/W_o against time are shown in figure 59. The initial order is changed in this representation; the initial rate, Cl'/W_o per min., is highest for polymer CD2 and the other polymers have approximately equal rates. The change in relative rates with increasing time is more apparent in this figure and the same order as before would be obtained at infinity, i.e., Cl'/W_o for CD4 < CD2 < CD1 < CD3.

TABLE 39. RELATIVE Cl'/W_o VALUES AT 200°C.

Time of degradation	Cl'/W_o (%)			
min.	CD1	CD2	CD3	CD4
10	1.10	2.00	0.91	1.20
30	2.14	3.18	1.88	2.27
60	3.60	4.43	3.06	3.20
120	5.40	5.65	4.97	3.51
240	8.04	7.66	7.42	4.38

FIGURE 59. DEGRADATION OF CHLORINATED POLYMERS AT 200°C.



When the temperature of degradation is varied and the time interval kept constant (figure 60), it becomes obvious that the relative stabilities depend on the temperature of degradation used. Thus, polymer CD4 is the least stable polymer at 190°C and the most stable at 240°C; the order of stabilities at 190°C, as measured by the ratio, Cl'/Cl_o, is the reverse of the order at higher temperatures (>250°C). These peculiar kinetic features are discussed further in terms of mechanism later in this chapter.

Kinetic order and activation energy.

The results of degradation of these chlorinated polymers (tables 30-33) could not be fitted to any simple kinetic pattern. Since many polymers exhibit first order kinetics during at least part of their degradation,[38] first order tests were applied to the degradation data. This is exemplified for polymer CD1 in figure 61 in which the logarithm of the function, $100(1 - Cl'/Cl_o)$, is plotted against time. This function is equivalent to the percentage residue (cf. pages 123-125). The graphs were not linear but it was conceived that the curves might be divisible into two linear portions corresponding to the fast and slow reactions in a concurrent reaction scheme;[125] kinetics of this type have been observed for chlorinated butyl rubber,[73] the fast and slow reactions being assigned to the

FIGURE 60. COMPARISON OF Cl/Cl_o - TEMPERATURE CURVES.
(TIME OF DEGRADATION - 100 MINUTES).

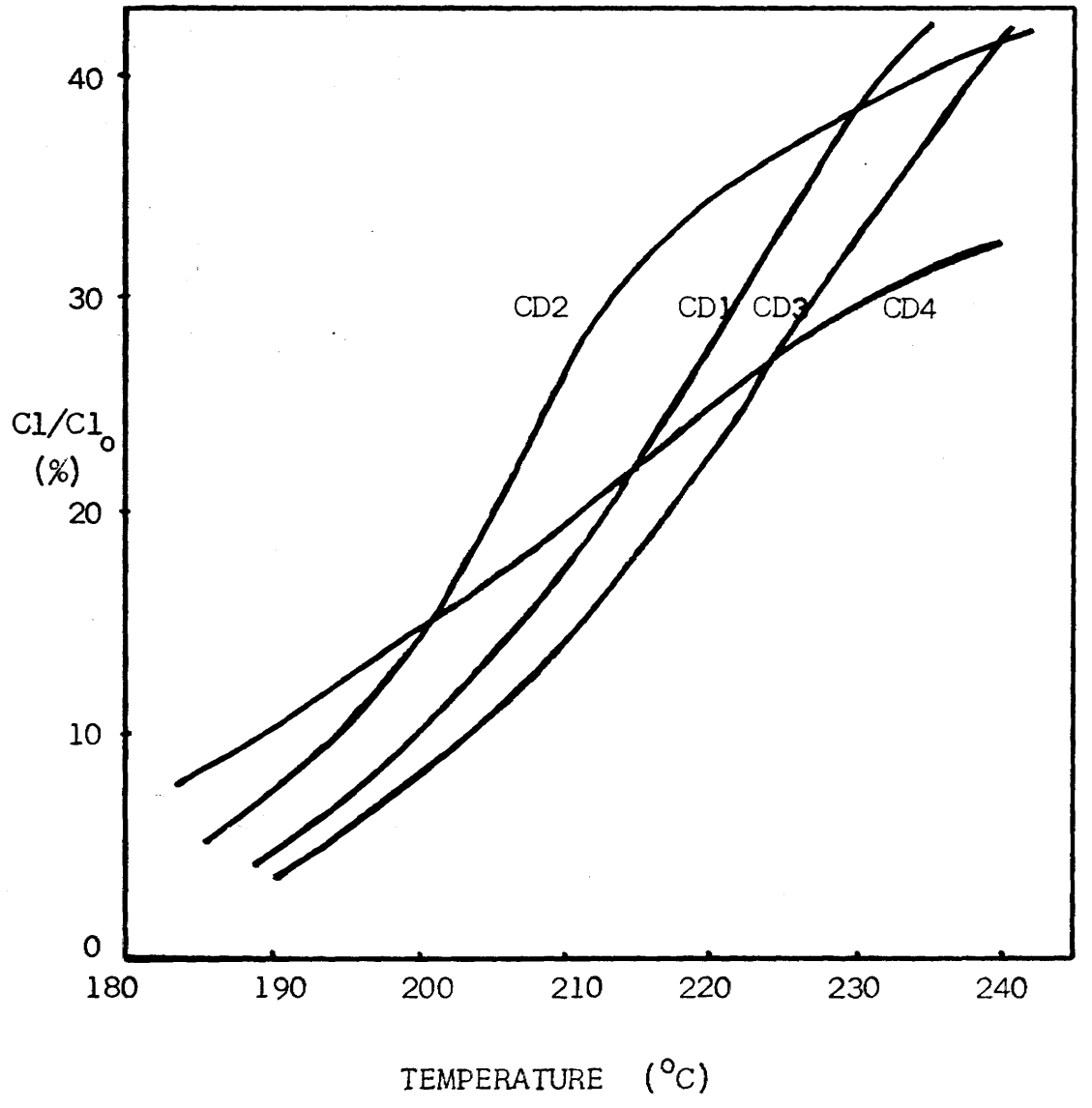
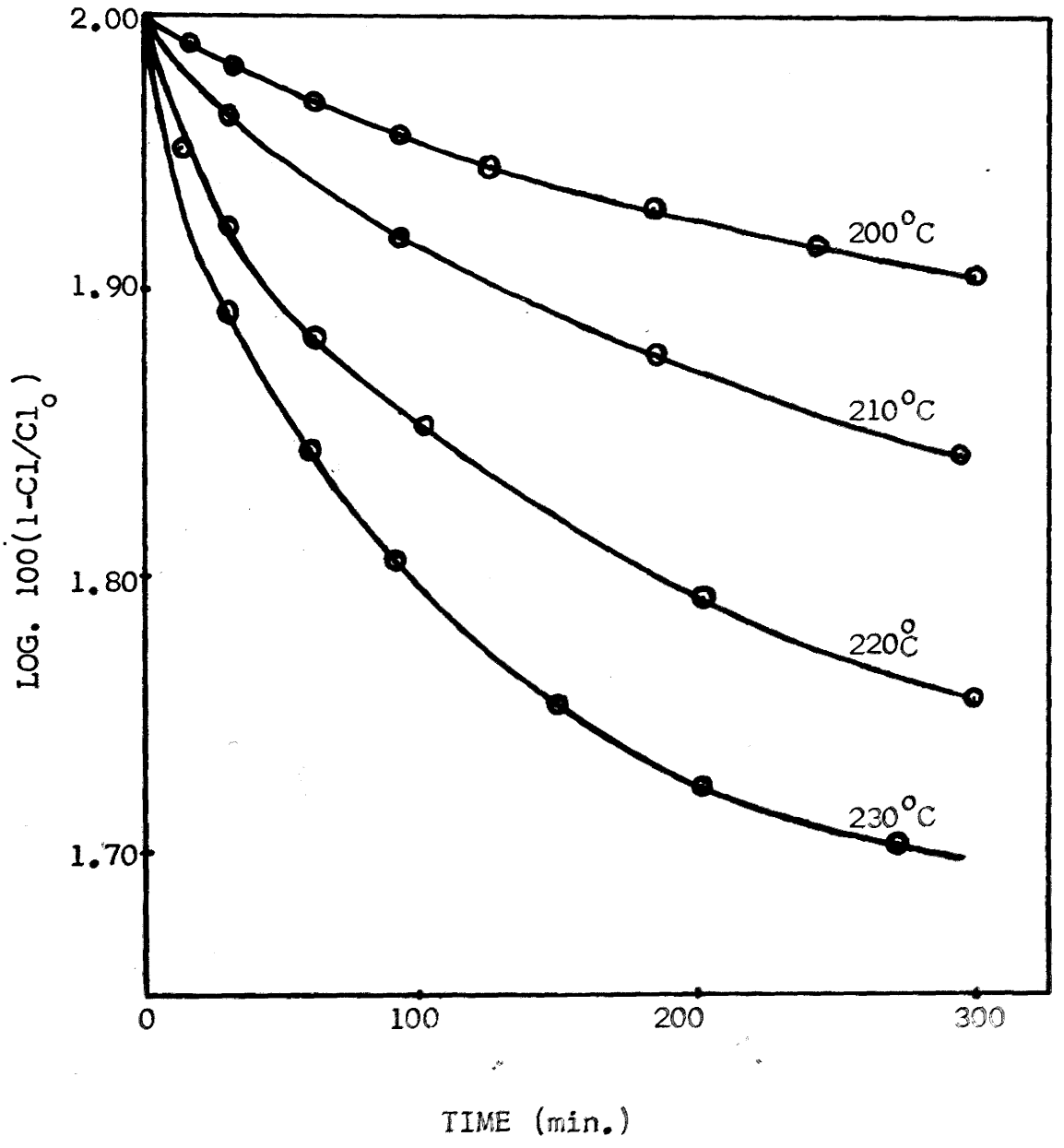


FIGURE 61. TEST FOR 1ST. ORDER KINETICS FOR POLYMER CD1.



loss of tertiary and secondary chlorine atoms respectively. In the present study, however, the curves did not acquire linearity within the 300 minute period of degradation and after this time the change in Cl/Cl_o was of the same order as the experimental error, and could not therefore be accurately measured.

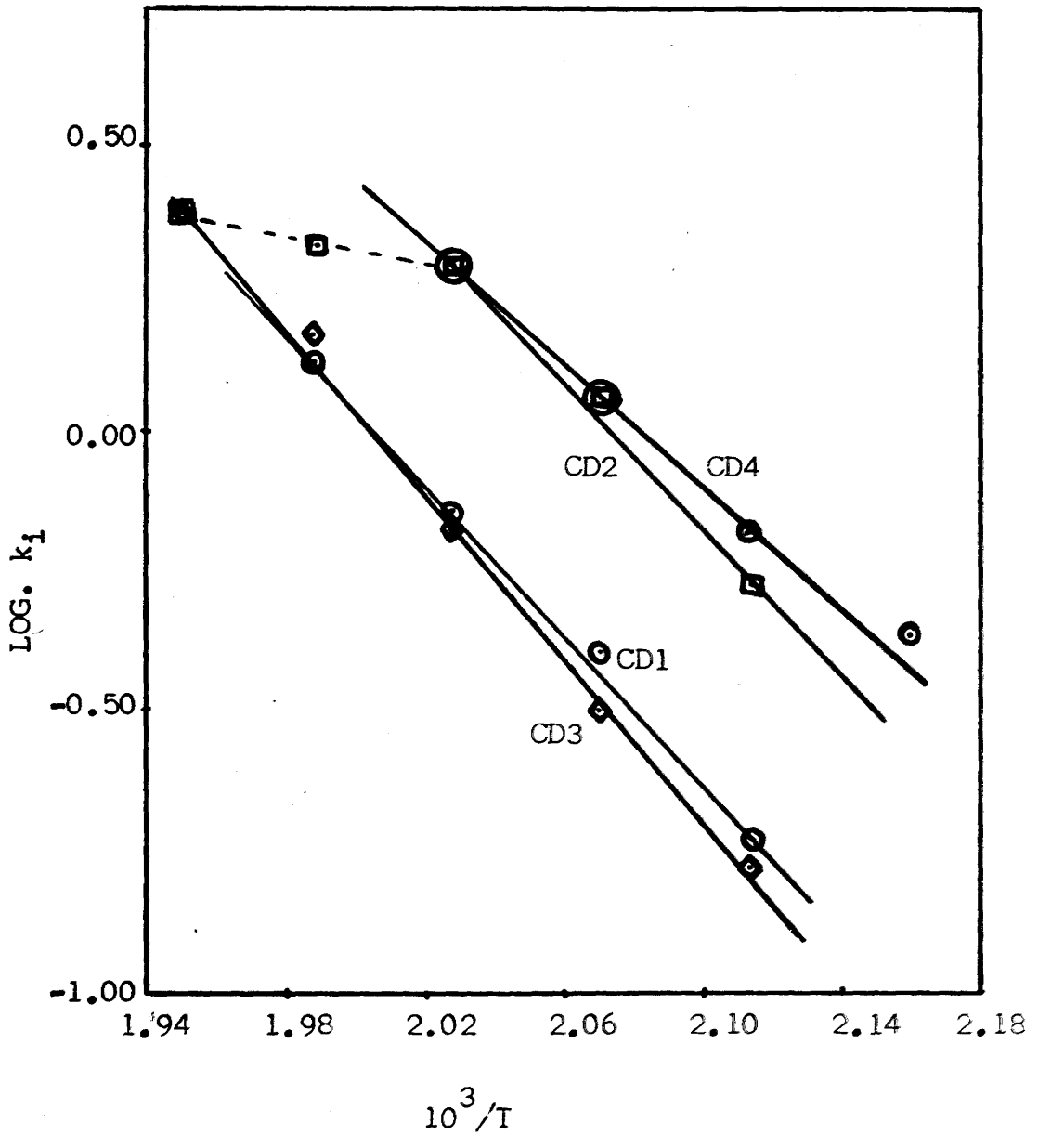
Approximate values of the activation energy were obtained from the initial rates. These were difficult to measure accurately since the rate decreased rapidly from an initial maximum. For polymer CD2 the initial rates were so steep that the mean rates over the first ten minutes of degradation were used instead of the initial rates. The measured initial rates are given in table 40 and the Arrhenius-type plots of the data are shown in figure 62. The activation energies derived from this treatment (cf.page 119) are presented in table 41. The values of E_A were in the range $30 \pm 5 K.cal.mole^{-1}$. The value observed for polymer CD4 was lower than the others, but, since the data used was approximate, it cannot be concluded whether this is a real difference or simply a reflection of the experimental error. The value of $30 k.cal.mole^{-1}$ is lower than that expected for an initiation step involving C-Cl fission[3] so that initiation probably involves labile structures. It is possible also that in these polymers the C-Cl scission is assisted by steric factors since chlorine atoms have been

TABLE 40. INITIAL RATES OF DEGRADATION AT VARIOUS TEMPERATURES.

Temperature °C	Temperature °A	$10^3/T$ $(°A)^{-1}$	Initial rate (k_i) $100Cl'/Cl_o$ / min.			
			CD1	CD2*	CD3	CD4
190	463.2	2.160	-	-	-	0.44
200	473.2	2.114	0.19	0.54	0.17	0.66
210	483.2	2.070	0.40	1.15	0.32	1.15
220	493.2	2.028	0.72	1.95	0.67	2.00
230	503.2	1.988	1.32	2.10	1.50	-
240	513.2	1.949	-	2.56	2.63	-

* Mean rates over first 10 minutes of degradation.

FIGURE 62. ARRHENIUS PLOTS OF INITIAL RATES.



substituted into a chain which was already sterically strained owing to the pairs of bulky methyl groups.

TABLE 41. ACTIVATION ENERGIES FROM FIGURE 62.

	CD1	CD2	CD3	CD4
Slope from Fig.62. x 10^{-3}	-6.7	-7.2	-7.2	-5.6
E_A k.cal.mole^{-1}	30.6	33.0	33.0	25.6

Since the degradation of the polymers consisted mainly of HCl evolution and since dehydrochlorination may follow a fractional order as in P.V.C. degradation,[45] the results were treated for fractional orders such as 1/2, 3/2, etc. These tests were mainly unsuccessful, but for an order of 3/2 a curious feature emerged; the equation for a 3/2 order reaction is:

$$- dC/dt = kC^{3/2}$$

which on integration yields;

$$C^{-½} = C_o^{-½} + ½kt .$$

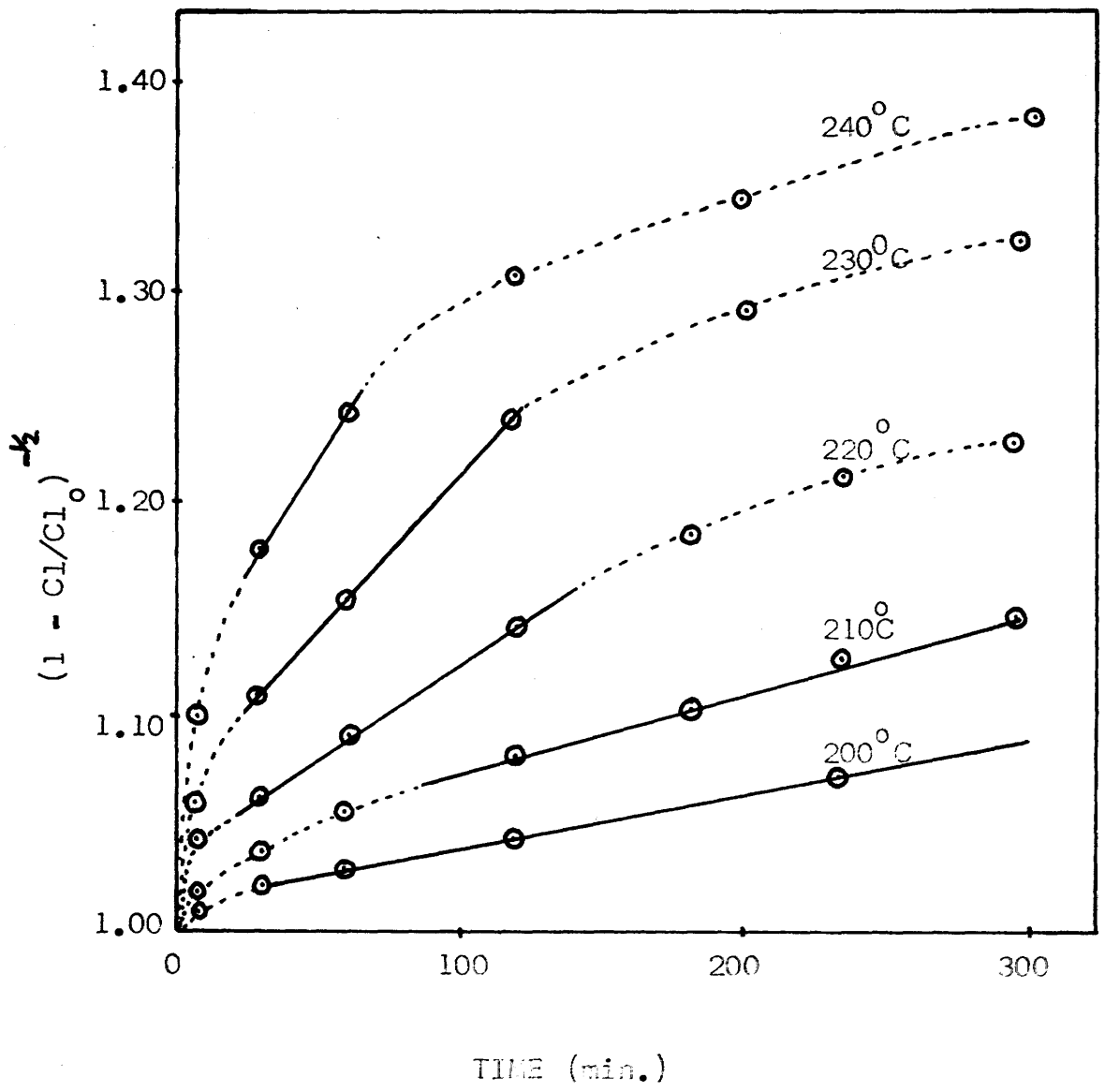
The concentration term, C, can be represented by $(1 - Cl'/Cl_o)$ i.e., the fraction of chlorine remaining in the polymer. When the function, $(1 - Cl'/Cl_o)^{-½}$, was plotted against time, it was found that the middle parts of the curves were linear.

This is illustrated in figure 63 for polymer CD3 which showed the linearity better than the other polymers. The linear portion of each curve was more evident at lower temperatures; at the upper temperatures of 230-240^{o}C, the linear part was barely noticeable. For polymer CD3, it was possible to derive a value of the activation energy from the slopes of the linear portions using the Arrhenius treatment (pages 119,218). The value obtained was 26 k.cal.mole^{-1}. From this evidence, it was concluded that part of the degradation behaviour was consistent with a free-radical reaction involving HCl formation. On the whole, however, it appears that the kinetic order is masked in these degradations; a plausible explanation is that part of the degradation mechanism involves a reaction which stabilises the product. Thus, the specific rate of HCl formation tends to decrease as the product becomes increasingly stabilised. Eventually, the evolution of HCl is completely inhibited although the polymer still contains appreciable amounts of chlorine (at least 40%).

Mechanism of Degradation.

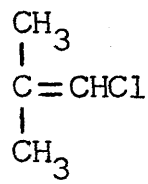
It is difficult to conceive a satisfactory mechanism which would account for all the observations presented in this chapter. The difficulty is increased by the irregularity of the polymer structure with respect to the chlorine

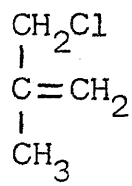
FIGURE 63. TEST FOR $3/_2$ ORDER FOR POLYMER CD3.



substituents. It would have been advantageous to have studied model chlorinated polyisobutenes of exact structure, but the required monomers,

1-chloro-2-methyl propene and 2-methyl-3-chloro-propene, (methallyl chloride)





do not polymerise to form high polymers.

Since the main volatile product was HCl and a kinetic order of 3/2 seemed applicable to part of the degradation curves, P.V.C. was considered as a possible model, but in the present system the chain reaction forming HCl in P.V.C.[39,45] is impossible and the analogy breaks down at the propagation step in which the chlorine atom is regenerated,i.e.,

$$\text{P.V.C.} \xrightarrow{\text{Initiation}} \text{Radical} + Cl^{\bullet} \quad \ldots\ldots(1)$$

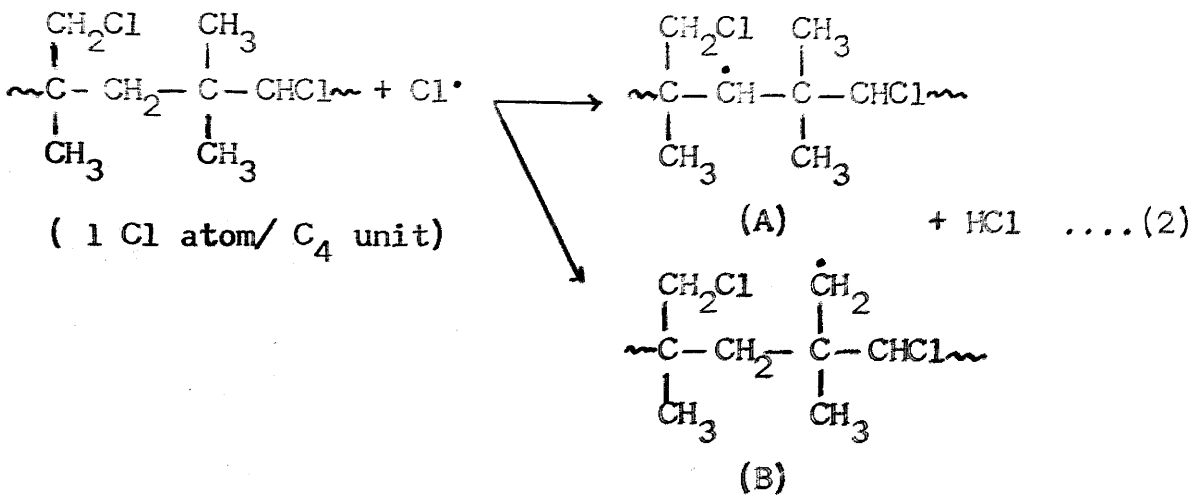
$$\sim CH_2-CHCl-CH_2-CHCl\sim + Cl^{\bullet} \longrightarrow \sim CH_2-CHCl-\dot{C}H-CHCl\sim + HCl \quad \ldots\ldots\ldots(2)$$

$$\sim CH_2-CHCl-\dot{C}H-CHCl\sim \longrightarrow \sim CH_2-CH=CH-CHCl\sim + Cl^{\bullet} \quad \ldots(3)$$

For chlorinated polyisobutene, the initial step of C-Cl fission can again be postulated, i.e.,

$$\text{Polymer} \xrightarrow{\text{Initiation}} \text{Radical} + Cl^{\bullet} \quad \ldots\ldots\ldots(1)$$

The liberated chlorine atom abstracts a nearby hydrogen atom:



(1 Cl atom/ C_4 unit)

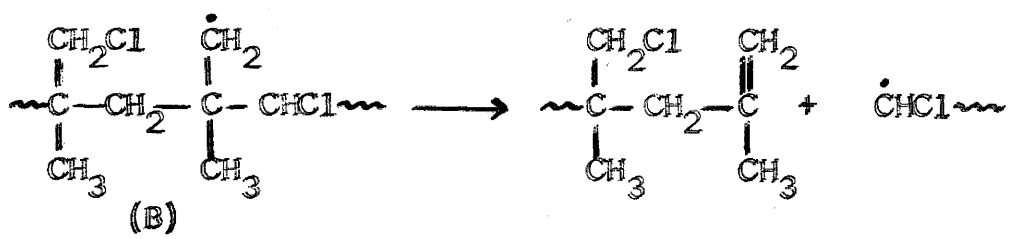
(A) + HCl ....(2)

(B)

There is no adjacent chlorine atom available to complete the cycle so that other reactions of the radicals A and B must be considered:

1. Chain Scission:

This appears to occur in the initial stages of degradation since an initial fall in molecular weight was observed, (table 34).



(B)

2. Transfer or Unzipping Reactions:

These reactions would lead to the formation of low M.W. chlorinated molecules; since these were minor products,

the amount of unzipping must be small. Isobutene is formed by unzipping through non-chlorinated sections of the polymers. It would be expected that transfer would be suppressed by the steric and electronic influences of adjacent chlorine and methyl substituents.

3. Combination:

If the radicals do not react by depropagation or transfer they must react with each other by combination. Intermolecular combination, i.e., cross-linking, would counteract the effect of scission reactions, thus explaining why the M.W. tended to remain approximately constant after the initial stages of degradation. Intramolecular combination would result in cyclisation and would not affect the molecular weight.

The study of the relative stabilities of the four polymers showed that the initial rate was highest for the polymer of lowest chlorine content. This probably depends on the hydrogen abstraction step. The formation of HCl depends not only on the fission of a C-Cl bond but also on this chlorine atom removing a hydrogen atom from a neighbouring methyl or methylene group. As the degree of chlorination increases, this latter process would be hindered by neighbouring chlorine atoms shielding the

hydrogen atoms. The number of unsubstituted methyl and methylene groups available would be smaller for polymers of high chlorine content so that again hydrogen abstraction would become increasingly difficult.

Another striking feature of the degradation was that the evolution of HCl ceased after 40-60% loss of chlorine from the polymer. Whether this results from cross-linking or cyclisation is uncertain although it is known that it is more difficult to remove chlorine from a cross-linked polymer.[58] Definite proof of cross-linking does not emerge from the present study. An alternative explanation is that only part of the substituted chlorine is labile in the temperature range, 200-240°C. The chlorine in the $-CCl_2-$ units would be expected to be less stable than that in the -CHCl- and $-CH_2Cl$ units[126], most of which appeared to be intact after several hours of degradation at 200°C (P.M.R. spectra). Chlorine atoms allylic to double bonds also form labile units and these could in fact be produced during degradation owing to chain scission reactions.

Oxygenated structures present in the polymer could also form initiation centres for degradation; the presence of small amounts of such structures was indicated by the I.R. spectra of the residues and by the fact that an oxygenated compound was found in the volatile products. The presence of cyclic and aromatic structures, e.g., styrene, was

suspected from the mass-spectrometric study of the volatiles. It is exceedingly difficult to relate such structures to the initial chlorinated and branched hydrocarbon chain; if styrene was a true product, gross fragmentation of the chains must occur during degradation. If this happened, the development of colour in the residues could be rationalised in terms of conjugated double-bond sections; the I.R. spectra, however, did not show appreciable double bond formation so that the mechanism of colouration remains obscure.

CONCLUSION.

The principal features of the thermal degradation of chlorinated derivatives of polyisobutene can be summarised as:

1. The chlorinated polyisobutenes degraded at lower temperatures than the parent polyisobutene owing to the relative instability of the C-Cl bonds, but were more stable than other chlorinated polymers such as P.V.C. and poly(vinylidene chloride) since the hydrogen and chlorine could not be split out from adjacent carbon atoms in the chlorinated polyisobutene chain.
2. Dehydrochlorination was the main process at temperatures below 250°C, but small amounts of other products, e.g., isobutene, C_4H_7Cl, indicated that some unzipping and

fragmentation reactions took place.

3. The kinetic order of the degradation was masked by stabilisation of the polymer prior to complete loss of chlorine, but an order of 3/2 was applicable to part of the degradation curves. The activation energy was approximately 30 k.cal.mole^{-1}. Rates of degradation decreased rapidly from an initial maximum.

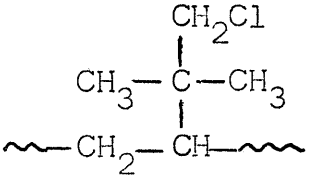
4. The stabilisation of the polymers could be due to cross-linking reactions, but another feasible explanation is that only part of the chlorine content is labile at the temperatues of degradation used.

5. Since the hydrogen and chlorine could not be eliminated from adjacent carbon atoms, no marked instability was observed for the polymer containing one chlorine atom per original monomer unit, cf., P.V.C., chlorinated polypropylene.[58] Polyisobutenes with less than one chlorine atom per monomer unit were in fact the least stable initially so that it was concluded that the ease with which the chlorine atom could migrate and abstract a hydrogen atom was an important factor in the kinetics of degradation.

6. A yellow residue remained even after prolonged degradation at temperatures below 250^{o}C, but further decomposition could be induced by heating to higher temperatures. Thus, polymers of low chlorine content were

completely volatilised at 500°C (Chapter 5), but polymers of chlorine content greater than 45% degraded to a black residue which was involatile at 500°C. The mechanism of the colour formation and the changes in the polymer structure on forming the residue could not be deduced from the methods of analysis employed, i.e., I.R. and P.M.R. spectroscopy.

This work could be most usefully extended, and additional insight gained into some of the aspects still to be resolved, by studying other chlorine-containing polymers of regular structure, containing chain units which appear in chlorinated polyisobutene. Although the ideal models, methallyl chloride and 1-chloro-2-methyl propene, do not polymerise, it should be possible to make polymers containing similar structures,e.g.,



A polymer of this structure would have all the chlorine atoms in a known position and still retain the essential feature that the carbon atom adjacent to the chlorinated group has no hydrogen atom available for 1:2 HCl elimination.

REFERENCES.

1. Norrish and Russell, Trans. Faraday Soc.,48,91 (1952).
2. Burnett, Mechanism of Polymer Reactions, Interscience, New York-London, 1954, Ch.3.
3. Grassie, Chemistry of High Polymer Degradation Processes, Butterworths, London, 1956 (p.29-33).
4. Oakes and Richards, J.Chem.Soc.,4,2929 (1949).
5. Turner, J.Polymer Sci.,A2, 1699 (1964).
6. Horning and Marvel, Synthetic Polymers in Organic Chemistry, an Advanced Treatise, Gilman (Ed.),Vol.1,754, Wiley, New York, 1943.
7. Jungnickel and Polgar, Organic Analysis, Vol.3, 203-386, Kolthoff,Mitchell,Proskauer and Weissberger(Ed.), Interscience, New York, 1956.
8. Kolthoff, Lee and Mairs, J. Polymer Sci.,3,66(1948).
9. Johnson, Kolthoff and Lee, Analyt. Chem.,22,995(1950).
10. Kemp and Peters, Ind. Eng. Chem.(Analyt.),15,453(1943).
11. Gallo, Nelson and Weise, Ind. Eng. Chem.,40,1277(1948).
12. Buckwalter and Wagner, J.Amer.Chem.Soc.,52,5241(1930).
13. Hagan and Thinius, Trans.J.Plastics Inst.,34(109),11,(1966).
14. Albertson and MacGregor, Analyt.Chem.,22,806(1950).
15. Pepper and Reilly, Proc.Chem.Soc.,1961,460.
16. Brown, Brown and Sivasankaran, J.Org.Chem.,28,214(1963).
17. Rehner, Ind. Eng. Chem.,36,118(1944).
18. Gray and Rehner, Ind.Eng.Chem.(Analyt.),17,367(1945).
19. Kolthoff and Lee, J.Polymer Sci.,2,206(1947).

20. Johnson and Saffer, Ind.Eng.Chem.,40,538(1948).

21. Gol'denberger and Lyubetskii, Polymer Sci.USSR., 4(2),1627(1963).

22. Stanescu, Rev. Chim.(Bucharest), 19,42(1963).

23. Rugg, Smith and Wartman, J.Polymer Sci.,11,1(1953).

24. Ketelaar, Salomon, Van der Schee and Van Eyk, Discussions Faraday Soc., 9,291(1950).

25. Richardson and Sacher, J.Polymer Sci., 10,353 (1953).

26. Binder, Analyt. Chem., 26,1877(1954).

27. Hampton, Analyt. Chem., 21,923(1949).

28. Barnes, Liddel and Williams, Ind.Eng.Chem.(Analyt), 15, 83 (1943).

29. McNeill, Polymer, 4, 15 (1963).

30. Cuta and Kucera, Chem. Abstracts, 48, 3850 (1954).

31. Haider, M.Sc. Thesis, Glasgow, 1966.

32. Makhdumi, M.Sc. Thesis, Glasgow, 1964.

33. Flett and Plesch, J. Chem. Soc., 1952, 3355.

34. Plesch (Ed.), Chemistry of Cationic Polymerisation, Pergamon Press Ltd., 1963, Ch.4.

35. Polymer Degradation Mechanisms, Circular 525, National Bureau of Standards, 1953.

36. Jellinek, Degradation of Vinyl Polymers, Academic Press, New York, 1955.

37. Thermal Degradation of Polymers, Society of Chemical Industry, Monograph No.13, London, 1961.

38. Madorsky, Thermal Degradation of Organic Polymers, Polymer Reviews No.7, Interscience, 1964.

39. Grassie, Chemical Reactions of Polymers, Fettes (Ed.), Interscience, 1964, p.565-644.

40. Grassie and Melville, Proc. Roy. Soc., A199, 1(1949).

41. Brown and Wall, J. Phys. Chem., 62, 848(1958).

42. Blatz, Simha and Wall, J.Polymer Sci., 5, 615(1950).

43. Simha and Wall, J.Polymer Sci., 6, 39 (1951).

44. Simha and Wall, J.Phys. Chem., 56, 707 (1952).

45. Achhammer, Straus and Stromberg, J.Polymer Sci., 35, 355 (1959).

46. Pezzin and Talamini, Makromol. Chem., 39, 26 (1960).

47. Baum and Wartman, J.Polymer Sci., 28, 537 (1958).

48. Arlman, J.Polymer Sci., 12, 543 (1954).

49. Winkler, J.Polymer Sci., 35, 3 (1959).

50. Grassie, Trans. Faraday Soc., 48,379(1952); 49,835(1953).

51. Grant and Grassie, Polymer, 1, 445 (1960).

52. Grassie and McNeill, J.Chem. Soc., 3, 3929 (1956).

53. Grassie and McNeill, J.Polymer Sci., 30, 37 (1958).

54. Madorsky and Straus, J.Res.Nat.Bur.Standards, 53,361(1954).

55. McIntyre, O'Mara and Straus, J.Res.Nat.Bur.Standards, 68A, 153 (1964).

56. Winslow, Baker and Yager, Proc. First and Second Conferences on Carbon, Feb. 1956, 93-102.

57. Amagi and Murayama, J.Polymer Sci., 4B, 115 (1966).

58. Krentsel, Seminido and Il'ina, Polymer Sci. USSR., 4(2), 1232, 1239 (1963).

59. Sorenson and Campbell, Preparative Methods in Polymer Chemistry, Interscience, New York-London, 1961, 190-192.

60. Burge, Ehrmantraut, Steele and Walker, Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, 1963.

61. Farish, Ph.D. Thesis, Glasgow, 1965.

62. Flory and Fox, J. Amer. Chem. Soc.,70,2384(1948); J. Phys. Chem., 53, 197 (1949).

63. McNeill, J. Chem. Soc., 1961, 639.

64. Faires and Parkes, Radioisotope Laboratory Techniques, Newnes, London, 1958.

65. McNeill, Ph.D. Thesis, Glasgow, 1957.

66. McNeill, Polymer, 4, 247 (1963).

67. Findlay, Practical Physical Chemistry, Longmans, Green & Co London, 1954, p.354.

68. McNeill, private communication.

69. Thompson and Torkington, Trans. Faraday Soc.,41,246(1945).

70. Matusevich and Slobodin, Polymer Sci. USSR.,4, 1487 (1963).

71. Dainton and Sutherland, J. Polymer Sci., 4, 37 (1949).

72. Biddulph, Plesch and Rutherford, J. Chem. Soc.,1965, 275.

73. Baldwin, Buckley, Kuntz and Robinson, Rubber Plastics Age, 42, 500 (1961).

74. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953, 273-274.

75. Sheshukov, J. Russ. Phys. Chem. Soc., 16, 478 (1884).

76. Eschard, Kuriacose and Mayer, Bull. Soc. Chim.(Fr.), 1961, 624.

77. Streigler, Chem. Tech.(Berlin), 9, 523 (1957).

78. Burgin, Engs, Groll and Hearne, Ind.Eng.Chem.,31,1413(1939)

79. Poutsma, J. Amer. Chem. Soc., 87, 2172 (1965).

80. Groll, Hearne, Rust and Vaughan, Ind.Eng.Chem.,31,1239(1939

81. Hinman and Poutsma, J. Amer. Chem. Soc., 86, 3807 (1964).

82. Poutsma, J. Amer. Chem. Soc.,87, 2161,4285,4293 (1965).

83. Hawkins and Philpot, J. Chem. Soc.,1962, 3204.

84. Chambers, Prickett, and Reeve, J.Amer.Chem.Soc.,74,5369(195

85. Taft, J. Amer. Chem. Soc., 70, 3364 (1948).

86. Dewar and Fahey, J. Amer.Chem.Soc., 85, 2248 (1963).

87. Ingold, Structure and Mechanisms in Organic Chemistry, Cornell University Press, Ithaca, New York, 1953, p.658.

88. Kennedy and Thomas, J. Polymer Sci.,A1, 331 (1963).

89. Norrish and Russell, Nature, 160, 543 (1947).

90. Biddulph and Plesch, J. Chem. Soc., 1960, 3913.

91. Reference 34, p.181.

92. Reference 35, p.234.

93. Cameron, Private communication.

94. Barrel, Johnson and Porter, J. Chromatog., 11, 177 (1963).

95. Wall, J. Res. Nat. Bur. Standards, 41,315 (1948).

96. Madorsky, Straus, Thompson and Williamson, J. Polymer Sci., 4, 639 (1949).

97. Golubtsova, Dokl.Akad.Nauk.SSSR., 84, 701 (1952).

98. Brady, Huff and McBain, J.Phys.Coll.Chem., 55, 304(1951).

99. Inoue, Ouchi and Yasuhira, Chem. High Polymers (Japan), 13, 31 (1956).

100. Kriukova, Moiseev and Neiman, Inst.Chem.Phys., 1, 1552 (1959).

101. Madorsky, J.Polymer Sci., 9, 133 (1952).

102. Jellinek, J.Polymer Sci., 4, 13 (1949).

103. Jellinek, Reference 35.

104. Thomas, Trans. Faraday Soc., 57, 511 (1961).

105. Dolgoplask, Kuren'gina, Tinyakova and Yerusalimskii, Izvest.Akad.Nauk.SSSR.,Otd.Khim.Nauk.,1960, 312.

106. Alexander, Black and Charlesby, Proc.Roy.Soc.(London), A232, 31 (1955).

107. Wall, J.Polymer Sci., 17, 306 (1955).

108. Turner, J.Polymer Sci.,A2, 1699 (1964).

109. Brown, Madorsky, Simha, Straus and Wall, J.Amer.Chem.Soc.,76, 3430 (1954).

110. Straus and Wall, J.Polymer Sci.,44, 313 (1960).

111. Van Schooten and Wijga, Reference 37, p.432.

112. MacCallum, Makromol. Chem., 83, 129 (1965).

113. Miller and Morway, U.S. patent 2,181,144 (Std.Oil Dev).

114. Sparks and Thomas, U.S. patent 2,275,164 (Std.Oil Dev).

115. Hahn and Grafmuller, Makromol. Chem., 21, 121 (1956).

116. Jackman, Applications of N.M.R. Spectroscopy in Organic Chemistry, Pergamon Press, New York, 1959.

117. Grassie, Torrance, Fortune and Gemmel, Polymer, 6, 653 (1965).

118. Grassie, McNeill and McLaren, J.Polymer Sci., 3B, 897 (1965).

119. McCall and Slichter, Newer Methods of Polymer Characterisation, Ke(Ed.), Interscience, 1964, Ch.8.

120. Owens and Zimmerman, J.Polymer Sci., 1A, 2711(1963).

121. Backsai and Lapporte, J.Polymer Sci., 1A, 2225(1963).

122. Tiers, Minnesota Mining and Manufacturing Co. publication, project 737,602, 1958.

123. Satoh, J.Polymer Sci., 2A, 5221 (1964).

124. Hawkins, Stoll, Thomas and Willholm, Helv. Chim. Acta, 46, 2098 (1963).

125. Frost and Pearson, Kinetics and Mechanism, Wiley, New York, 1953, 149.

126. Havens, reference 35.